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CHEMILUMINESCENT MATERIALS

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DECEMBER 1, 1963 - FEBRUARY 29, 1964

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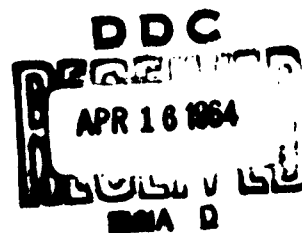
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SUMMARY

Progress in determining the processes fundamental to chemilumi-
nescence is described with primary reference to the oxalyl chloride-
hydrogen peroxide-fluorescent acceptor chemiluminescent reaction, chemi-
luminescent decomposition of anthracene photoperoxides, synthetic approaches
to new potentially chemiluminescent compounds, and energy transfer in
chemiluminescent systems. Five new chemiluminescent reactions related to
peroxyoxalic acid decompositions are reported with a correlation suggest-
ing that the formation of excited carbon dioxide is common to all. A
stable, solid chemiluminescent composition based on oxalic acid is
described. The emitting species in peroxyoxalic acid chemiluminescence
has been shown to be the singlet excited state of the fluorescent
acceptor present in the system. Preliminary energy transfer studies in
the peroxyoxalic acid system are described. Additional work is expected
to define the transfer mechanism.

Energy transfer experiments with the 3-aminophthalhydrazide-
fluorescein system have demonstrated the occurrence of non-radiative
energy transfer, but the extent of transfer will require quantitative
measurement with a more suitable acceptor.

A new investigation of the mechanism of anthracene photoperoxide
chemiluminescence is discussed, and the synthesis of specific compounds for
study is described.

Continuing efforts to prepare certain peroxidic acridine deriva-
tives and azo anthracenes are reported; several of the desired acridines
are expected to be available during the fourth quarter.

Continuing efforts to prepare a chemiluminescent phthal-
hydrazide polymer and a highly fluorescent phthalhydrazide have been
successfully completed. However, quantitative chemiluminescence
measurement of each of the materials indicated that the sought-for
improvement in chemiluminescence efficiency was not obtained.

INTRODUCTION

On the following pages is presented the third quarterly technical progress report on a project designed to provide a detailed understanding of the processes fundamental to chemiluminescence. The subject matter is organized in essentially the same format used in the preceding reports. To avoid repetition, the objectives of a particular study are described in complete detail only in that report where the study is introduced. With the exception of the investigation of anthracene photoperoxide chemiluminescence discussed in Section I B, this report describes work introduced in earlier reports.

SECTION I

REACTION MECHANISMS IN CHEMILUMINESCENCE

A. The Reaction of Oxalyl Chloride with Hydrogen Peroxide in the Presence of a Fluorescent Acceptor.

Oxalyl chloride has been reported to react vigorously with hydrogen peroxide to produce carbon monoxide, oxygen, and hydrochloric acid with little emission of light[1]. When carried out in the presence of a fluorescent compound, however, the reaction generates a bright light at least approximately matching the normal fluorescence emission of the fluorescent compound[1].

$$Cl\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}Cl + H_2O_2 \xrightarrow{\quad anthracene \quad} CO + O_2 + \diagup anthracene \diagdown *$$

$$\diagup anthracene \diagdown * \xrightarrow{\hspace{3cm}} anthracene + light$$
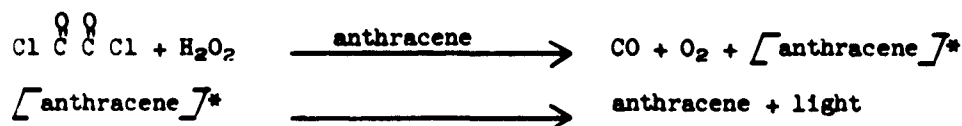
This reaction is of substantial interest because of the implied energy transfer process whereby chemical energy produced by the oxalyl chloride-hydrogen peroxide reaction appears as singlet electronic excitation energy in the fluorescent compound. The reaction is also unusual in that organic chemiluminescence is customarily derived from more complex systems.

An adaquate description of the over-all mechanism requires answering fundamental questions dealing with: (1) the chemical mechanism of the process involving oxalyl chloride which leads to the generation of electronic excitation energy, and (2) the mechanism of the process by which the energy appears as the singlet excited state

of the fluorescent acceptor. Our program is currently investigating both of these areas. The experimental work bearing on the second question is primarily spectroscopic and will be discussed in Section III.

The preceding report[2] presented experimental evidence bearing on the chemical process, which was tentatively interpreted in terms of the following free radical chain mechanism:

$$1. \quad Cl\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}Cl + H_2O_2 \longrightarrow Cl\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}OOH + HCl \quad (I)$$

$$2. \quad Cl\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}OOH + H_2O_2 \longrightarrow HOO\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}OOH + HCl \quad (II)$$

$$3. \quad HOO\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}OOH + R\cdot \longrightarrow RH + O_2 + CO + CO_2 + HO\cdot$$

$$4. \quad HO\cdot + HOO\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}OOH \longrightarrow O_2 + CO + CO_2 + HO\cdot + H_2O$$

$$5. \quad Cl\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}Cl + H_2O \longrightarrow 2HCl + CO + CO_2$$
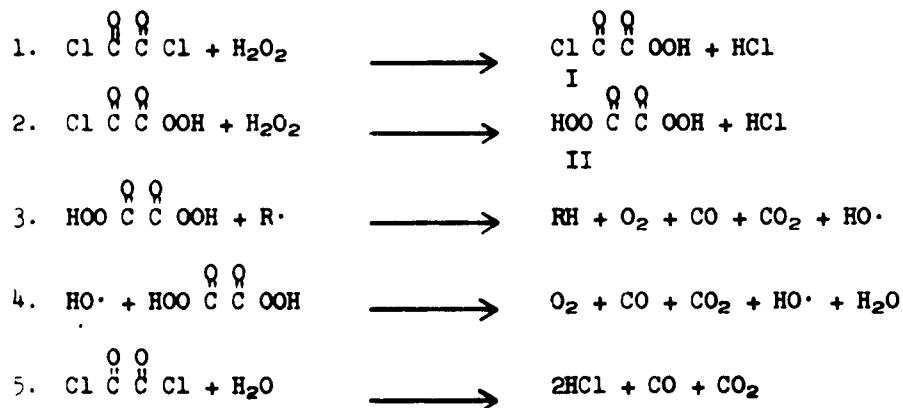
The evidence suggesting this mechanism[2] is summarized below.

(a) The maximum amount of light is generated when hydrogen peroxide rather than oxalyl chloride is used in excess indicating the essential formation of intermediate II.

(b) The free radical inhibitor 4-methyl-2,6-di-t-butylphenol suppresses chemiluminescence and gas evolution for five to ten minutes when added to a glowing reaction mixture in ether, indicating a free radical chain reaction.

(c) The stoichiometry of the reaction is one to one in oxalyl chloride and hydrogen peroxide.
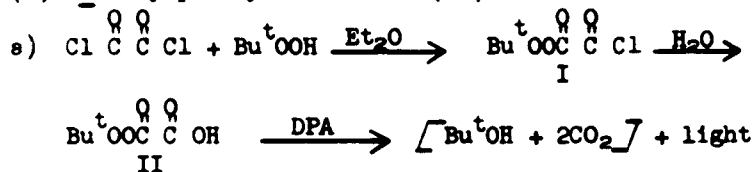
(d) The reaction of oxalic acid with hydrogen peroxide and dicyclohexylcarbodiimide, which would be expected to provide II as an intermediate, was found to be chemiluminescent in the presence of a fluorescent compound.

Additional work designed to further clarify the chemical process has led to the following results:
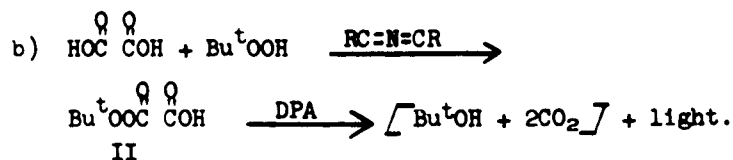
New Chemiluminescent Reactions

In order to define the essential structural features of the key intermediate in the chemiluminescent reaction several variations of the oxalyl chloride-hydrogen peroxide reaction were investigated.

(1) t-Butylperoxyoxalic Acid (II)

$$a)\quad Cl\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}Cl + Bu^tOOH \xrightarrow{Et_2O} Bu^tOO\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}Cl \xrightarrow{H_2O}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad I$$

$$Bu^tOO\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}OH \xrightarrow{DPA} \big[Bu^tOH + 2CO_2\big] + light$$
$$\qquad II$$

Reaction of oxalyl chloride with t-butylhydroperoxide in the presence of 9,10-diphenylanthracene in ether does <u>not</u> product light, indicating that neither the monoperoxide, I, nor di-t-butyldiperoxy-oxalate, $Bu^tOO\overset{O}{\underset{}{C}}\overset{O}{\underset{}{C}}OOBu^t$, is a chemiluminescent material. However, addition of water to an ether solution of I prepared <u>in situ</u>, provides a moderately bright emission, probably derived from decomposition of t-butylperoxyoxalic acid (II) formed by hydrolysis of I. An attempt to prepare a sample of I free from oxalyl chloride according to a procedure in the literature[3] ended in an explosion. An additional attempt will be made.

b) $\overset{O\ O}{HOC\ COH}$ + Bu^tOOH $\xrightarrow{\ RC=N=CR\ }$

$Bu^t\overset{O\ O}{OOC\ COH}$ $\xrightarrow{\ DPA\ }$ $\sqrt{\ Bu^tOH\ +\ 2CO_2\ }$ + light.
II

Reaction of oxalic acid with t-butylhydroperoxide and dicyclo-hexylcarbodiimide in the presence of 9,10-diphenylanthracene provides a moderately bright chemiluminescence, again probably derived from t-butylperoxyoxalic acid, II.

Decomposition of II by a free radical chain reaction is possible, and such a process would lead to the formation of t-butyl alcohol and carbon dioxide but not oxygen or carbon monoxide. Bartlett and Pincock indicate that t-butyl alcohol and carbon dioxide are indeed the sole products of t-butylperoxyoxalic acid decomposition[3]. While these assumptions remain to be varified by gas analysis and inhibitor experiments under the conditions used here, the result suggests that carbon dioxide is the essential product of the chemiluminescent process. Experiment (b) also indicates that monoperoxyoxalic acid, $HOO\overset{O\ O}{C\ COH}$, rather than diperoxyoxalic acid may be involved in the corresponding reaction with anhydrous hydrogen peroxide.

(2) Ethyl Hydroperoxyoxalate (III)

$C_2H_5O\overset{O\ O}{C\ C}Cl$ + H_2O_2 $\longrightarrow$ $C_2H_5O\overset{O\ O}{C\ COOH}$ $\xrightarrow{\ DPA\ }$
III

$\sqrt{\ C_2H_5OH\ +\ O_2\ +\ 2CO\ }$
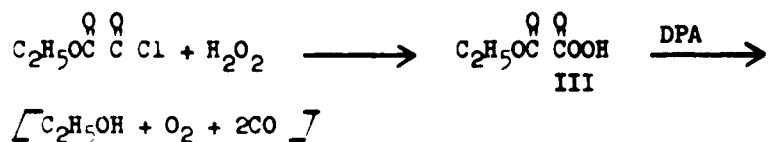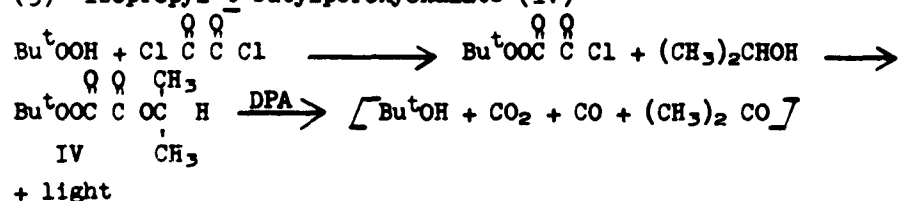
Reaction of ethyl oxalyl chloride with hydrogen peroxide in the presence of 9,10-diphenylanthracene in benzene is not chemiluminescent at room temperature, although a very weak emission is observed at 80°.
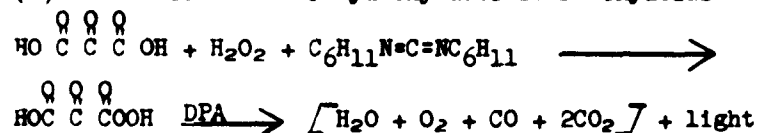
Since carbon dioxide would not be expected to be a substantial product of free radical chain decomposition of III, this result further indicates the importance of carbon dioxide formation in the chemiluminescent process. However, an alternative decomposition path is possible[3] which would produce carbon dioxide by a non-concerted bond cleavage. The reaction products will be determined in the near future.

(3) Isopropyl t-butylperoxyoxalate (IV)

$$Bu^tOOH + Cl \overset{O}{\underset{}{C}} \overset{O}{\underset{}{C}} Cl \longrightarrow Bu^tOO\overset{O}{\underset{}{C}} \overset{O}{\underset{}{C}} Cl + (CH_3)_2CHOH \longrightarrow$$

$$Bu^tOO\overset{O}{\underset{}{C}} \overset{O}{\underset{}{C}} O\overset{CH_3}{\underset{}{C}} H \xrightarrow{DPA} \underline{/}Bu^tOH + CO_2 + CO + (CH_3)_2 CO\underline{/}$$
$$\qquad IV \qquad CH_3$$
$$+ \text{ light}$$

Reaction of t-butylperoxyoxalyl chloride, prepared in situ, with anhydrous isopropyl alcohol in the presence of 9,10-diphenylanthracene provides a moderately strong chemiluminescent emission probably derived from free radical chain decomposition of IV. Corresponding reactions with anhydrous methanol or t-butyl alcohol were not appreciably chemiluminescent.

(4) Ketomalonic and Dihydroxytartaric Peroxyacids

$$HO \overset{O}{\underset{}{C}} \overset{O}{\underset{}{C}} \overset{O}{\underset{}{C}} OH + H_2O_2 + C_6H_{11}N=C=NC_6H_{11} \longrightarrow$$

$$HOC \overset{O}{\underset{}{C}} \overset{O}{\underset{}{C}} \overset{O}{\underset{}{C}} COOH \xrightarrow{DPA} \underline{/}H_2O + O_2 + CO + 2CO_2\underline{/} + \text{light}$$

Both ketomalonic and dihydroxytartaric acids generated light when added to anhydrous hydrogen peroxide and dicyclohexylcarbodiimide. The corresponding monoperoxy acid is probably the key intermediate in each case.

(5) Phosgene Derived Reactions

The following reactions, carried out in ether in the presence of 9,10-diphenylanthracene, were not chemiluminescent.

a) $Cl \overset{O}{C} Cl + H_2O_2 \longrightarrow Cl \overset{O}{COOH} \overset{?}{\longrightarrow} HO\overset{O}{OC} OOH \overset{?}{\longrightarrow}$

$$HCl+O_2+CO \qquad H_2O+O_2+CO_2$$

b) $C_2H_5O\overset{O}{C} Cl + H_2O_2 \longrightarrow C_2H_5O\overset{O}{C}OOH \overset{?}{\longrightarrow}$

$$[C_2H_5OH + O_2 + CO]$$

c) $Cl \overset{O}{C} Cl + Bu^tOOH \longrightarrow Bu^tO\overset{O}{OC} Cl + H_2O \longrightarrow$

$$Bu^tOO\overset{O}{C}OH \overset{?}{\longrightarrow} [Bu^tOOH + CO_2]$$

d) $Bu^t OO\overset{O}{C} Cl + (CH_3)_2CHOH \longrightarrow$

$$Bu^tOO\overset{O}{C} O\overset{CH_3}{\underset{CH_3}{C}-H} \longrightarrow [Bu^tOH + CO_2 + (CH_3)_2CO]$$
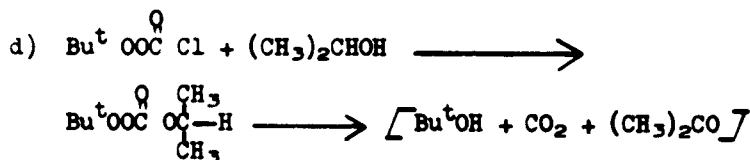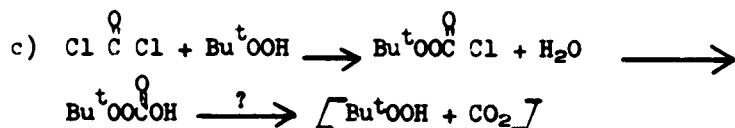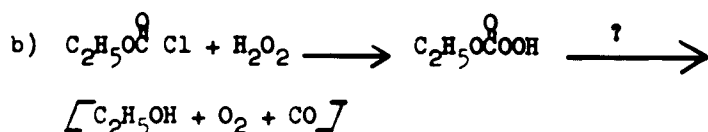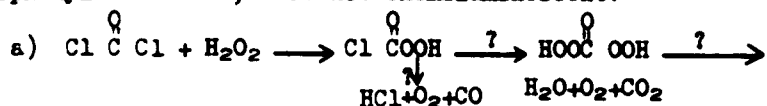
Reaction Conditions for Oxalic Acid Chemiluminescence

Acidic Catalysts. As noted in the previous report[2], methane sulfonic acid increases the intensity of the oxalic acid-dicyclohexyl-carbodiimide-anhydrous hydrogen peroxide-fluorescent acceptor chemi-luminescent reaction. Additional studies have indicated that acetic acid, p-nitrobenzoic acid, phosphoric acid and p-toluene sulfonic acid are equally effective. The effect of acids in increasing the intensity thus appears to be general.

Dehydrating Agents. Chemiluminescence is obtained when mixtures of oxalic acid, anhydrous hydrogen peroxide, methane sulfonic

acid and 9,10-diphenylanthracene are warmed in benzene in the presence
of acetic anhydride, trifluoroacetic anhydride, or phenyl isocyanate.
Phosphorus pentoxide and phthalic anhydride were ineffective. None of
these dehydrating agents were effective in ether solution.

Solid Perhydrates. Anhydrous hydrogen peroxide can, as expected,
be replaced with urea peroxide or sodium pyrophosphate peroxide without
loss in intensity in the oxalic acid-carbodiimide chemiluminescent reac-
tion. Such solid sources of hydrogen peroxide accommodate the formula-
tion of solid chemiluminescent compositions. One such composition has
been prepared from oxalic acid, dicyclohexylcarbodiimide, sodium
pyrophosphate peroxide, p-toluenesulfonic acid, and 9,10-diphenylanthra-
cene. This composition has a shelf-life of at least ten weeks, and
provides moderately strong chemiluminescent emission when scratched on
a plate or when added to an organic solvent.

Solvents. The effect of solvents on the reaction of oxalic
acid with anhydrous hydrogen peroxide and acetic anhydride in the
presence of 9,10-diphenylanthracene is summarized in the following
chart.

Table I

Solvent	Oxalic Acid Solubility	Intensity*
benzene	part. sol.	medium
toluene	insol.	medium
hexane	insol.	medium strong
acetonitrile	part. sol.	very weak
acetone	sol.	weak
diglyme	sol.	medium strong
methanol	sol.	very weak
acetic acid	part. sol.	medium
dimethylformamide	sol.	weak

* A medium intensity corresponds approximately to the intensity of the aqueous 3-aminophthalhydrazide-H_2O_2-$K_2S_2O_8$ reaction.

9,10-Diphenylanthracene Photoperoxide

The reaction of oxalyl chloride with anhydrous hydrogen peroxide in ether in the presence of 9,10-diphenylanthracene photoperoxide is not chemiluminescent, demonstrating that 9,10-diphenylanthracene does not generate chemiluminescence through reversible transformation to its photoperoxide.

Analysis of Gaseous Products from Reactions of Oxalyl Chloride with Anhydrous Hydrogen Peroxide

Yields of gaseous products from reactions of oxalyl chloride with hydrogen peroxide in the presence of 9,10-diphenylanthracene under

varying conditions were estimated by measuring the volume and pressure of gas generated in a closed system, and analyzing the composition of the gas by mass spectrometry. The results are summarized in Table II.

Table II

Gaseous Products from Oxalyl Chloride-Hydrogen Peroxide Reactions

Oxalyl Chloride (millimoles)	Hydrogen Peroxide (millimoles)	Solvent		Conversion Based on Oxalyl Chloride		
				CO^a	CO_2^a	O_2^b
4.93	4.90	ether	15 ml	38.2	47.0	1.8
5.00^c	5.00	ether	15 ml	46.5	46.8	7.0
4.93^d	4.90	ether	15 ml	37.3	45.8	2.0
5.35	4.90	dimethyl-phthalate	15 ml	25.0	71.2	0.13
5.35^d	4.90	dimethyl-phthalate	15 ml	25.9	69.5	0.05
5.35	9.80	dimethyl-phthalate	20 ml	30.7	69.3	0.05
5.35^d	9.80	dimethyl-phthalate	20 ml	44.0	57.1	0.33

[a] Percent conversion of oxalyl chloride carbon. Complete consumption of oxalyl chloride was always noted; additional hydrogen peroxide did not produce additional light.

[b] Moles of oxygen as a percentage of oxalyl chloride.

[c] This reaction was allowed to age 36 min. following the end of light emission before sampling the evolved gases. All other experiments were sampled one to two min. after chemiluminescence had ceased.

[d] One mole per cent based on oxalyl chloride of 4-methyl—2,6-ditertiarybutylphenol was present as a radical inhibitor.

As seen in the table, the experiments carried out in ether provided about one-half of the oxalyl chloride carbon as carbon dioxide. The carbon monoxide yield apparently depended on the reaction time before sampling, with a higher yield obtained after a longer period even though chemiluminescent emission was always complete before sampling. This effect will be rechecked. The maximum carbon monoxide yield is evidently about fifty per cent. The experiments carried out in dimethyl-phthalate solution gave substantially more carbon dioxide and correspondingly smaller yields of carbon monoxide. The use of excess hydrogen peroxide did not significantly alter the yields. Reasonable carbon balances were obtained in most experiments in spite of the approximate nature of the mass spectrometric analysis. As indicated in the table very little oxygen was found in any of the experiments. However, a possible error appeared in the mass spectrometric oxygen interpretation and these results will be rechecked by a gas chromatographic technique.

In three of the experiments 4-methyl-2,6-di-$\underline{t}$-butylphenol was added to study the effect of free radical inhibition on product yields. An effective radical inhibitor would be expected to delay the peroxide decomposition process beyond the period necessary to complete the formation of the peroxide by ionic reactions. As seen in Table I, the inhibitor had no significant influence on product yields in those experiments where equimolar quantities of oxalyl chloride and hydrogen peroxide were used. In one inhibitor experiment where excess hydrogen peroxide was used, the ratio of carbon monoxide to carbon dioxide was

substantially higher. Chemiluminescence observation of the inhibitor experiment in ether confirmed our earlier report[2] that the inhibitor causes a pronounced induction period. In the present experiment the induction period lasted about five minutes and was abruptly followed by strong chemiluminescent emission concurrent with vigorous gas evolution. The effect of the inhibitor in the dimethylphthalate experiments was far less pronounced with moderately strong emission and smooth gas evolution occurring throughout the reaction.

The gas analysis results in ether solution are in reasonable agreement with the diperoxyoxalic acid-free radical chain mechanism tentatively proposed, since the low yield of oxygen can be explained by a rapid radical-initiated autooxidation of ether. Rapid autooxidation of dimethylphthalate, however, would not be expected[4] and our preliminary failure to find oxygen in these experiments indicates that oxygen may not in fact be an important reaction product. The formation of carbon monoxide in these reactions indicates that the over-all process follows a different course than that observed in the decomposition of di-t-butyldiperoxyoxalate where essentially all of the oxalyl carbon appears as carbon dioxide[5].

The marked difference in inhibitor activity observed between ether and dimethylphthalate solutions may stem from the different chain carriers active in the solutions. In ether solution the expected chain carrier would be the radical $CH_3\dot{C}HOCH_2CH_3$ produced by hydrogen abstraction from ether or its autooxidation product, $CH_3\underset{OO\cdot}{CH}OCH_2CH_3$.

In dimethylphthalate solution the much more active hydroxyl radical would seem to be involved. The ether-derived chain carrier would be less active, more selective, and thus more efficiently trapped by an inhibitor present in low concentration. The effect of ether as a solvent in these reactions appears related to an observation by Bartlett and co-workers that an induced decomposition of di-t-butyldiperoxyoxalate occurs in ether solution but not in other solvents[5]. The effect of ether and the fate of the missing oxygen in these reactions will be studied in more detail.

B. Anthracene Photoperoxides

The key step in every chemiluminescent process is the specific step that generates the electronically excited emitting species. It is this step that one must understand in order to understand chemiluminescence. In most chemiluminescent reactions this key step is obscured by preceding and subsequent steps and by competing non-luminescent side reactions. The chemiluminescent thermal decomposition of anthracene photoperoxides, however, shows promise as a reaction accommodating the direct study of the key step. Since a number of these decompositions are reported to regenerate the corresponding anthracene and oxygen exclusive of other products, the decomposition would seem to be a single step process where the liberated anthracene appears as its excited state concurrent with the separation of oxygen.

V   VI
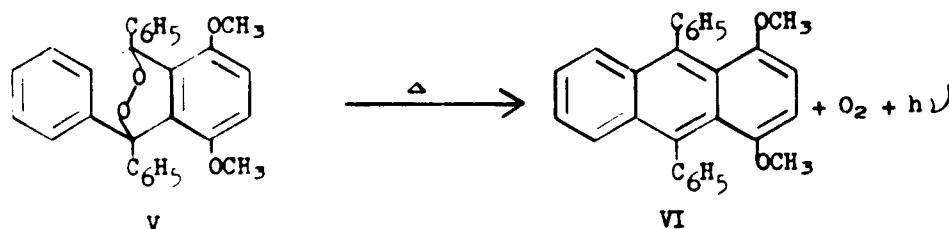
A comprehensive survey of the photoperoxide literature has been recently completed. References were obtained from Chemical Abstracts between 1954 and 1962 under the headings: anthracene photo-oxide: oxide, photo; oxidation, photo of .... Earlier references were obtained from review articles[6,7,8,9,10]. The field of photoperoxide chemistry was pioneered by Dufraisse[6] over thirty years ago, and there

are now nearly 200 references in the literature on this subject. Representative examples of decomposition temperatures and oxygen yields of photoperoxide decompositions are given in Tables III and IV. Attention is focused at once on two groups of photoperoxides; the 9,10-diphenyl-anthracene photoperoxides (50-60 derivatives have been made and studied) and the 1,4-dialkoxy anthracene photoperoxides. These two groups are believed to be the most promising photoperoxides from the point of view of chemiluminescence. The values summarized in these tables should be considered approximate, since the information has been compiled from varied sources and non-rigorous criteria of determination were generally used.

Table III

Anthracene Photoperoxide	$T_{dec.}(°C)$	$O_2\%$	Reference
$9,10$-di-C_6H_5	180	98	11
$9,10$-di-C_6H_5-1-OCH_3	150	89	12
$9,10$-di-C_6H_5-2-OCH_3	160-170	93	13
$9,10$-di-C_6H_5-1,4-di-OCH_3	25	82(98 at 80°C)	11,14
$9,10$-di-C_6H_5-1,4-di-OC_2H_5	70-75	95	14
$9,10$-di-C_6H_5-1,4-di-$OCH_2C_6H_5$	95-100	95	14
$9,10$-di-C_6H_5-1,2-di-OCH_3	135-140	40-72	15
$9,10$-di-C_6H_5-1,8-di-OCH_3	215	72	16
$9,10$-di-C_6H_5-2,3-di-OCH_3	120-150	95	15
$9,10$-di-C_6H_5-2,6-di-OCH_3	170-180	97	16
$9,10$-di-C_6H_5-1,4-di-CH_3	170	56	17
$9,10$-di-C_6H_5-1-CH_3-4-OCH_3	180	3 (+CO_2)	18
$9,10$-di-C_6H_5-1,4-di-Cl	195-200	77	19
$9,10$-di-C_6H_5-1-OCH_3-4-Cl	180	89	12
$1,4,9,10$-tetra-C_6H_5	200-210	87	19
$9,10$-di-C_6H_5-1,4-di-SCH_3	145-150	13	20
$9,10$-di-C_6H_5-1,4-di-SC_6H_5	145-150	32	20

Table $\underline{IV}$

Anthracene Photoperoxide	$T_{dec.}(^{\circ}C)$	$O_2\%$	$t_{1/2}(hrs)$	Reference
Unsubstituted	120	0		24
9,10-di-C_6H_5	180	98		11
9,10-di-CH_3	not given	0		25
1,4-di-OCH_3	25		0.31	21
1,4-di-OCH_3-9-OCH_3	25		1.45	21
1,4-di-OCH_3-9-C_6H_5	25		2.3	21
1,4-di-OCH_3-9-CH_3	25		4.5	21
1,4-di-OCH_3-9,10-di-C_6H_5	25	82	50-60	11,14,21
1,4-di-OCH_3-9,10-di-CH_3	m.p. 227*			22
1,4-di-OCH_3-9-C_6H_5-10-CH_3	m.p. 174*			22
1,4-di-OCH_3-9,10-di-OCH_3	m.p. 239*			22
1,4-di-OCH_3-9,10-di-2-pyridyl	80	95		23

* Stable at m.p.

The main points from the literature are summarized briefly below.

1. In general, only minor attention has been paid to the chemiluminescence associated with the decomposition of photoperoxides. Reports of quantum yield measurements have not been found. However, 1,4-dimethoxy-9,10-diphenylanthracene photoperoxide has been stated to be the most efficient of the known photoperoxides[6].

2. Anthracene photoperoxide itself and its 9,10-dialkyl derivatives are reported to explode or yield resinous products but not oxygen on heating[7]. In direct contrast the thermal decomposition of 9,10-diarylanthracene photoperoxides yield oxygen and parent anthracene as the only identifiable products. The oxygen produced by the decomposition of a large number of substituted anthracene photoperoxides has been determined and found to vary between 0-98%, as indicated in Tables III and IV. Not more than 98% of the theoretical oxygen could be accounted for in a number of attempts made with 9,10-diphenylanthracene photoperoxide. The oxygen yield is important. Unless the quantum yields of these decompositions are found to be higher than the missing amount of oxygen, the possibility that the light producing step is associated with an unknown side reaction must be considered.

3. The instability of anthracene photoperoxides has commonly been defined only by the temperature of decomposition (Table III). However, in some cases crude rate measurements have also been carried out and half-lives reported (Table IV). The decompositions have been found to follow a first order rate law.

Substituents affect both the thermal decomposition and the chemiluminescence drastically. This point is borne out by the data in Tables III and IV. It is noted particularly (Table III) that 1,4-dimethoxy-9, 10-diphenylanthracene photoperoxide decomposes and is chemiluminescent at room temperature, whereas the other dimethoxy isomers decompose at much higher temperatures. Alkoxy groups in general when substituted in the

1,4-positions tend to lower substantially the decomposition temperature of anthracene as well as 9,10-diarylanthracene photoperoxides but fail to effect 9,10-dialkylanthracene photoperoxides similarly (Table IV).

Steric crowding does not influence the stability of the photoperoxide in a decisive way as a comparison of the data for 1,4-dimethoxy, diethoxy and dibenzyloxy photoperoxide show in Table III.

Rate measurements and calorimetric determinations have only been carried out on the decomposition of rubrene photoperoxide[26,27]. The values found are summaried below.

Δ H (Photoperoxide $\longrightarrow$ Rubrene + O_2) : -23 Kcal/mole

$k \times 10^2$ min^{-1} = 4.1 at 129.2°C

E_a (for decomp.) = 40 Kcal/mole

For a preliminary study of anthracene photoperoxide chemiluminescence, we are preparing anthracenes VI through XIII below for conversion to their photoperoxides.

VI   VII   VIII   IX

X   XI   XII   XIII
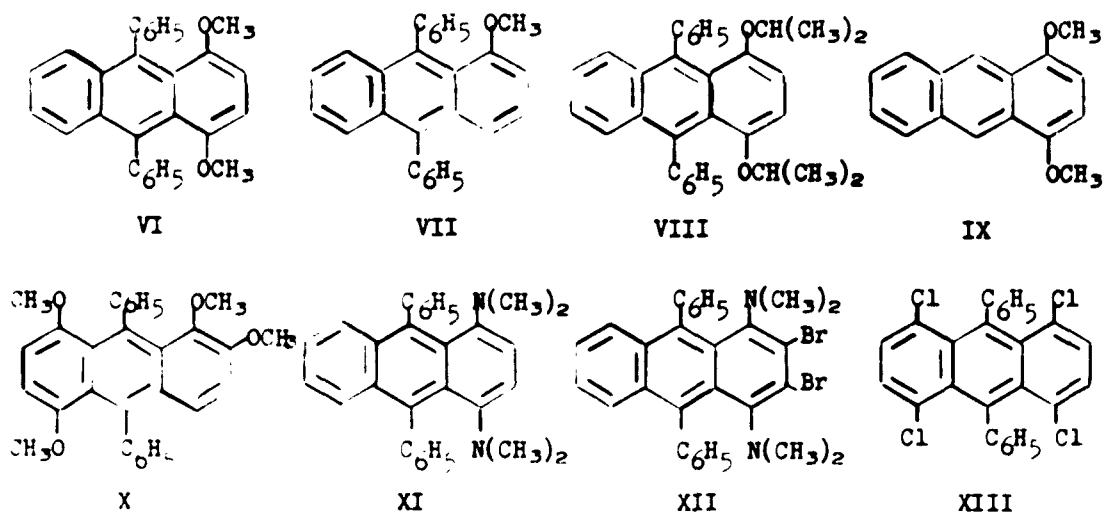
Selection of these particular compounds was based on the following criteria.

a) Known or expected chemiluminescence.

b) Low or moderate temperature of decomposition to facilitate quantitative determinations of products, quantum yields, and rates of decomposition. Moreover, a practical chemiluminescence system would also, in general, need to have low temperature of decomposition. This requirement eliminated both rubrene and photoperoxide and 9,10-diphenylanthracene photoperoxide.

c) Clean decomposition with a minimum amount of by-products. Side reactions would seriously complicate the study of both decomposition and chemiluminescence and impede the correlation of the critical light producing step with the corresponding chemical step.

d) Verification of substituent effects. Although the generally drastic effect of substituents on the decomposition of photoperoxides is known, it is poorly understood. The effect of substituents on chemiluminescence (e.g. on quantum yield) is not known.

e) Recent results[28] indicate that intersystem crossing from triplet to singlet states may play an important role in chemiluminescent reactions. Compound XII or XIII, whichever is more readily synthesized, will be used to test this possibility, since the heavy halogen atoms should facilitate intersystem crossing.
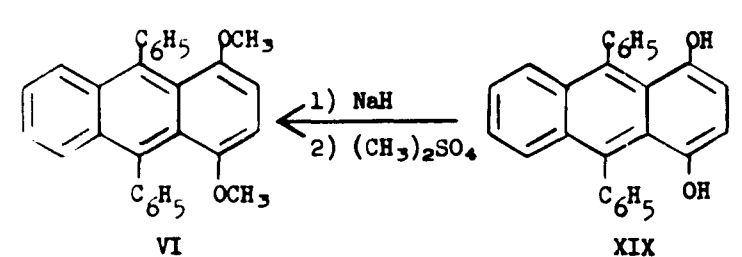
f) Ease of preparation.

Compounds VI, VII and IX have been prepared by the routes described below. The syntheses of X and XIII are in progress and are also described below.

1,4-Dimethoxy-9,10-diphenylanthracene (VI)

The procedure of Dufraisse[29] was used with substantial
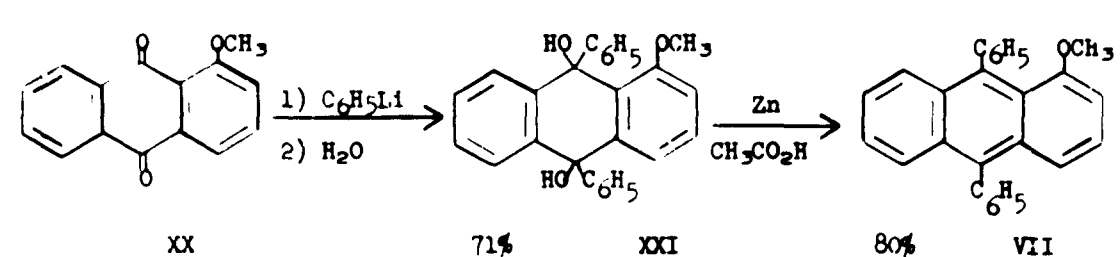
modifications.
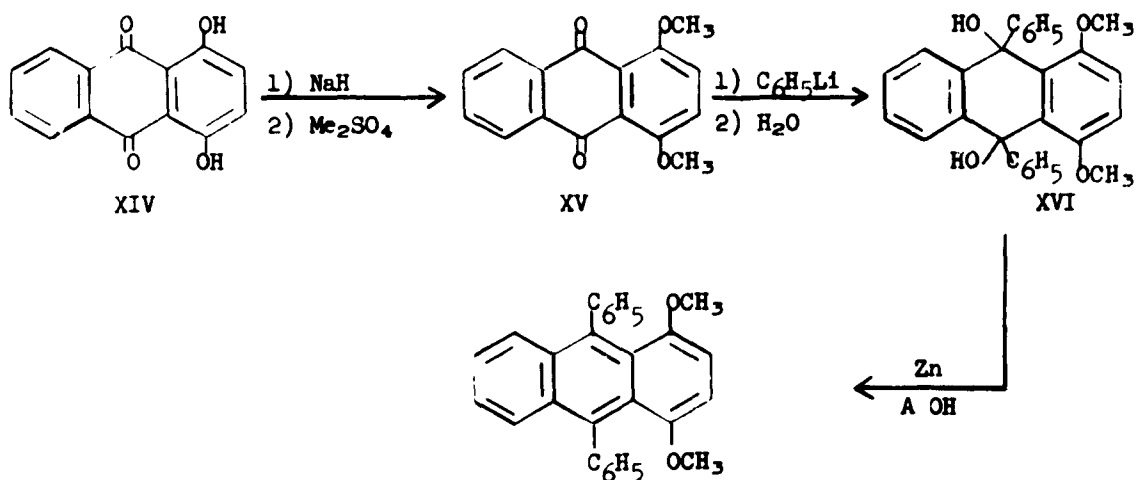
Poor yields ($\sim$11%) were obtained in the methylation of 1,4-

dihydroxyanthraquinone with sodium carbonate-dimethylsulfate, sodium

hydride-dimethylsulfate, or sodium hydride-methyliodide as methylating

agents. The reduction step with zinc also took place with low yield (16%).

A significant improvement in this step is expected by the addition of KI

or by the use of TCl$_3$ in methanol as reducing agent. However, another

possible route is also being tested to find a good way to accumulate suf-

ficient material.

This route involves the addition of phenyllithium to the dihydroxyquinone, dehydration to the 1,4-quinone in acidic medium, reduction to dihydroxyanthracene and eventual methylation of this anthracene. This second route avoids both low yield steps involved in the first synthesis.
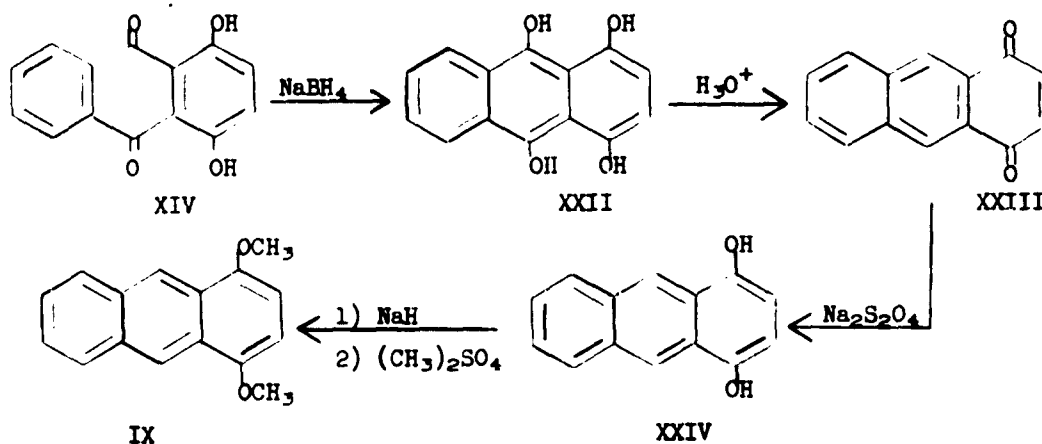
1-Methoxy-9,10-diphenylanthracene (VII)

The preparation was completed as indicated.

1,4-Dimethoxyanthracene (IX)

The procedure of Lepage[21] was used with minor modifications. No difficulties were encountered.

1,2,5,8-Tetramethoxy-9,10-diphenylanthracene (X)

The procedure starts with the methylation of 1,2,5,8-tetrahydoxy-anthraquinone to give the corresponding tetramethoxy quinone in analogy with the synthesis of compound VI. However, only partial methylation of the four hydroxy groups has been obtained so far. Further work awaits the result of the study on the preparation of compound VI described above.

1,4,5,8-Tetrachloro-9,10-diphenylanthracene (XIII)

XXV   XXVI

XIII
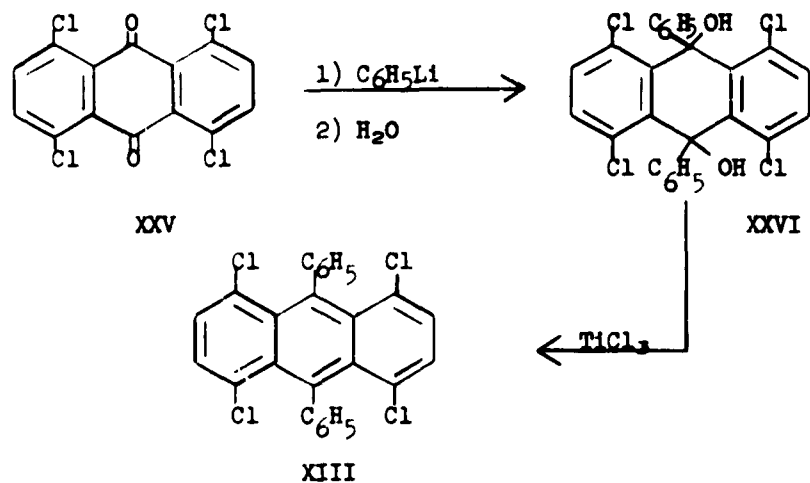
Tetrachloroanthraquinone was reacted with phenyllithium in good yield. However, the reduction of the dihydroxy compound to anthracene failed with zinc and will be attempted with $TiCl_3$.

SECTION I

EXPERIMENTAL

Tertiarybutylperoxyoxalyl Chloride Chemiluminescence. A solution of tertiarybutylperoxyoxalyl chloride in ether was prepared by adding 9.0 g. (0.1 mole) of tertiarybutyl hydroperoxide to 200 ml. of 1 M oxalyl chloride (0.2 mole) in ether over a 30 minute period. After standing an additional 30 minutes, aliquots of the solution were tested for chemiluminescence in the presence of 9,10-diphenylanthracene.

a. Addition of 5 drops of water to 25 ml. of test solution gave a strong blue chemiluminescence.

b. Addition of 5 drops of anhydrous 2-propanol to 25 ml. of test solution gave a medium blue chemiluminescence.

c. Anhydrous tertiarybutanol (5 drops) failed to give light when added to 25 m'. of the test solution.

d. Addition of 5 drops of anhydrous methanol to 25 ml. of test solution gave only a very weak chemiluminescence.

Tertiarybutylperoxyoxalic Acid. A solution of 2.1 g. (0.01 mole) dicyclohexylcarbodiimide in 10 ml. of ether was added to a mixture of 1.3 g. (0.01 mole) oxalic acid, 0.5 g. (0.005 mole) tertiarybutyl hydroperoxide, 5 drops of methane sulfonic acid and 5 mg. of 9,10-diphenylanthracene in 25 ml. ether. A bright blue chemiluminescence was observed.

Ethyl Oxalyl Chloride - H_2O_2 Reaction. Addition of 25 ml. of 0.64 M ethyl oxalyl chloride in ether to 25 ml. of 1 M anhydrous H_2O_2 in ether containing 9,10-diphenylanthracene failed to product light. Addition of the peroxide to the ethyl oxalyl chloride solution in another instance was also not chemiluminescent.

Ketomalonic Acid Chemiluminescence. A solution of 4.1 g. (0.02 mole) of dicyclohexyl carbodiimide in 25 ml. of ether was added to a mixture of 1.4 g. (0.01 mole) of the sodium salt of ketomalonic acid, 5 drops of methane sulfonic acid, and 5 mg. 9,10-diphenylanthracene in 25 ml. of 1 M H_2O_2 in ether. A bright blue chemiluminescence of about 30 seconds duration was produced.

Dihydroxytartaric Acid Chemiluminescence. A solution of 4.1 g. (0.02 mole) of dicyclohexylcarbodiimide in 25 ml. of ether was added to a mixture of 1.8 g. (0.01 mole) of dihydroxytartaric acid, 5 drops of methane sulfonic acid and 5 mg. of 9,10-diphenylanthracene in 25 ml. of 1 M H_2O_2 in ether. A bright brief blue chemiluminescence was observed.

Phosgene-Hydrogen Peroxide. Addition of 10 ml. of 1.2 $\underline{M}$ phosgene in benzene to 25 ml. of 1 $\underline{M}$ hydrogen peroxide in ether containing 5 mg. of 9,10-diphenylanthracene produced no light.

Ethyl Chloroformate + Hydrogen Peroxide. The addition of 25 ml. of 1 $\underline{M}$ ethyl chloroformate in ether to 25 ml. of 1 $\underline{M}$ hydrogen peroxide in ether containing 5 mg. of 9,10-diphenylanthracene failed to produce light. Addition of peroxide solution to ethyl chloroformate also gave no light.

Phosgene-Tertiary Butyl Hydroperoxide. A solution of 4.5 g. (0.05 mole) of tertiary butyl hydroperoxide in 10 ml. of benzene was added to 10 ml. (0.12 mole) of 1.2 $\underline{M}$ phosgene in benzene containing 10 mg. of 9,10-diphenylanthracene. No light was observed. The addition of 5 drops of water to 10 ml. of the reaction mixture produced no light. The addition of 5 drops of anhydrous isopropanol to the remaining 10 ml. of reaction mixture also failed to give light.

Acid Catalysts for Oxalic Acid Chemiluminescence. When 2.3 g. of dicyclohexyl carbodiimide in 7 ml. of ether was added to a mixture of 1 g. oxalic acid, 5 mg. 9,10-diphenylanthracene, and 5 drops of acetic acid in 25 ml. of 1 $\underline{M}$ H_2O_2 in ether, a bright blue chemiluminescence was observed. A similar result was obtained when 5 drops of phosphoric acid or 0.05 g. of para nitro benzoic acid or 0.05 g. of para toluene sulfonic acid were used in place of acetic acid.

Dehydrating Agents for Oxalic Acid Chemiluminescence. A mixture of 1 g. of oxalic acid, 2 ml. acetic anhydride, 5 mg. of 9,10-diphenylanthracene and 5 ml. of benzene was heated on the steam bath. No light was observed. On the addition of 1 ml. of 1 $\underline{M}$ H_2O_2 in ether to the mixture, a weak, long lived blue chemiluminescence occurred. The reaction also gave light when 2 ml. of trifluoroacetic anhydride or phenyl isocyanate was used in place of acetic anhydride.

Oxalic Acid Dry Powder Formula. An intimate mixture of finely ground oxalic acid (1.0 g., 0.008 moles), sodium pyrophosphate peroxide (6.0 g., 0.018 mole), para toluene sulfonic acid (0.5 g., 0.003 mole), dicyclohexyl carbodiimide (2.3 g., 0.011 mole), and 9,10-diphenyl-anthracene (0.05 g., 0.0002 mole) was prepared. When a portion of the mixture was scratched on a clay plate in the dark, a medium intensity blue luminescence was observed. Addition of the powder mixture to ether or to benzene also gave light. The mixture has a storage life of at least 12 weeks at room temperature.

Solvents for Oxalic Acid Chemiluminescence. A mixture of 1 g. of oxalic acid, 5 mg. of 9,10-diphenylanthracene, 2 ml. of acetic anhydride, and 5 ml. of solvent was heated on the steam bath then treated with 1 ml. of 1 $\underline{M}$ H_2O_2 in ether. The results are tabulated in Table I.

Gaseous Products from Oxalyl Chloride-Hydrogen Peroxide

Reactions. The experiments in Table I were carried out in an apparatus
consisting of a 500 ml. round bottom flask equipped with a magnetic
stirrer and fitted with an evacuated gas sample tube, a 10 ml. dropping
funnel, and a three-way stopcock leading to a differential manometer and
a vacuum pump. The total volume of the system was 620 ml. A solution
of hydrogen peroxide containing 10 mg. of 9,10-diphenylanthracene was
placed in the flask, cooled to -78°, and the system was evacuated. The
system was tested for leaks by isolating the system from the vacuum
pump at the stopcock and observing changes in the pressure by means of
the manometer. The cooling bath was removed and the oxalyl chloride
solution added to the system from the dropping funnel. When chemilumi-
nescence had ceased, the pressure of the system was read and a sample of
the gas was taken for analysis by mass spectroscopy. Gas evolution was
always concurrent with light emission. In experiments where an inhibitor
was present it was added with the peroxide solution.

Tertiary Butyl Peroxyoxalyl Chloride [5]. A solution of 4.5 g.

(0.05 mole) of tertiary butyl hydroperoxide in 40 ml. of anhydrous
hexane was added to a cold (0°C) solution of 12.6 g. (0.1 mole) of oxalyl
chloride in 40 ml. of anhydrous hexane during one hour. The solution was
then stirred for 2.5 hours at 0°. The solvent was removed at reduced
pressure using a dry-ice cooled collector flask and with an ice bath
around the product flask. When solvent removal was complete, the system
was pumped down to a pressure of 0.5 mm Hg and maintained there for 5
minutes in order to insure the removal of the last trace of oxalyl
chloride. On worming the product to room temperature a violent explo-
sion occurred destroying both product and apparatus.

1,4-Dimethoxyanthraquinone (XV). Quinizarin (1,4-dihydroxy-

anthraquinone) XIV (24 g., 0.1 mole) was dissolved in 300 ml. of dry
dimethylformamide. To this solution 12 g. (0.25 mole) 50% sodium
hydride disperion in a dry dimethylformamide was added slowly with
stirring. The deep violet solution which resulted was heated on a
steam bath for 1/2 hr. Then dimethylsulfate (15.8 g., 0.125 mole) was
added slowly to the stirred solution. The reaction mixture was kept on
a steam bath for 3 hrs., then diluted with 600 ml. of water and extracted
with four 500 ml. portions of benzene. The combined extracts were
washed with water, dried over magnesium sulfate, and evaporated to
dryness. The residue was collected, washed with 5% sodium hydroxide and
water, and dried to obtain 3.0 g. (11.2%) of product whose infrared
spectrum was in good agreement with that expected for the desired
product. This product was used directly in the next step without
further purification.

1,4-Dimethoxy-9,10-diphenyl-9,10-dihydroxy-9,10-dihydro-

anthracene (XVI). 1,4-Dimethoxyanthraquinone (4 g., 0.015 mole) was
added slowly to a stirred solution of 50 ml. of 2.4 M phenyl lithium

(Lithium Corporation of America) in 60 ml. tetrahydrofuran. The reaction mixture was stirred for 30 min. and allowed to stand for 2.5 hrs. Dilute acetic acid (60 ml., 10%) was added with stirring to the reaction mixture. The organic phase was separated, and the aqueous phase was extracted with three 150 ml. portions of ether. The combined organic solutions were washed with four 200 ml. portions of water, dried over magnesium sulfate, and evaporated to dryness to obtain 5.5 g. (86%) of product whose infra-red spectrum was in good agreement with that expected for the desired product. The material was used directly in the next step.

1,4-Dimethoxy-9,10-diphenylanthracene (VI). 1,4-Dimethoxy-9,10-dihydroanthracene (5 5 g., 0.013 mole) was refluxed for 45 min. with 12 g. of zinc powder in 300 ml. of glacial acetic acid. The reaction mixture was filtered hot, and water was added to the point of precipitation. Upon standing for 16 hrs., a black tarry material had separated, and was collected and dissolved in methanol. The solution was treated with activated charcoal, and evaporated to dryness to obtain 0.8 g. (16%) of yellow non-crystalline product, whose infrared spectrum was in good agreement with that expected for the desired product. After chromatography on neutral alumina a pale-yellow crystalline product was obtained, m.p. 189-191°C (Lit.[29] 202-203°C).

1-Methoxy-9,10-diphenyl-9,10-dihydroxy-9,10dihydroanthracene (XXI). 1-Methoxyanthroquinone (24 g., 0.1 mole) was added slowly with stirring to a solution of 330 ml. of 2.4 $\underline{M}$ phenyl lithium (Lithium Corporation of America) and 400 ml. tetrahydrofuran. The reaction mixture was stirred 30 min., then allowed to stand 2.5 hrs. at room temperature. Then aqueous acetic acid (400 ml., 10%) was added with stirring to the mixture. The organic phase was separated, and the aqueous phase extracted with four 250 ml. portions of ether. The combined organic solutions were washed with four 600 ml. portions of water, dried over anhydrous magnesium sulfate, and evaporated to dryness to obtain 28.1 g. (71.3%) of yellow-brown oily material whose infrared spectrum was in good agreement with that expected for the desired product.

1-Methoxy-9,10-diphenylanthracene (VIII). 1-Methoxy-9,10-diphenyl-9,10-dihydroxy-9,10-dihydroanthrace (28.1 g., 0.07 mole) was refluxed for 45 min. with 90 g. of zinc powder in 500 ml. of glacial acetic acid. The reaction mixture was filtered hot, and water was added to begin precipitation. A brown semisolid separated out on standing, and was collected and dissolved in benzene. The benzene solution was treated with activated charcoal, and evaporated to dryness to obtain 20 g. (80%) of product, whose infrared spectrum was in good agreement with that expected for the desired product. After chromatography on alumina and recrystallization from methanol, the light yellow product (51%) had a m.p. 178-179°C (Lit.[12] m.p. 176-177°).

1,4-Dimethoxyanthracene (IX). The procedure of Lepage[21] was used to obtain 11.0 g. (46%) of product, m.p. 131-134° (Lit.[21] m.p. 137°) whose infrared spectrum was in good agreement with that expected for the desired product.

SECTION II

STRUCTURAL CRITERIA FOR CHEMILUMINESCENT COMPOUNDS

Certain key questions bearing on the chemiluminescence process can best be answered by the design and synthesis of new potentially chemiluminescent compounds having appropriately selected structural features. Three such objectives of prime importantance have been described in the previous report[2]:

(A) Determination of essential structural characteristics required to provide an efficient mechanistic pathway for the conversion of chemical energy to electronic excitation energy.

(B) Determination of the effect of combining a highly fluorescent structure with a known chemiluminescent structure.

(C) Determination of the effect at high luminant concentration of incorporating a chemiluminescent structure into a polymeric backbone. The first objective deals with the basic mechanism of chemiluminescence. The second explores the possibility of increasing the efficiency of a known chemiluminescent reaction by increasing the fluorescent efficiency of the emitting species. The third objective attacks the general problem of efficiency loss at high luminant concentration.

## A. Formation of Electronically Excited Molecules

1. Relationship of peroxides to chemiluminescence

Attention has frequently been called to the fact that the known organic chemiluminescent reactions involve oxygen or hydrogen peroxide as a reactant. Indeed it has been shown that either oxygen or hydrogen peroxide is essential for appreciable chemiluminescence from 3-aminophthalhydrazide. These observations imply that organic peroxides are intermediates in the known systems. Thus while a variety of oxidizing agents will oxidize 3-aminophthalhydrazide, only oxygen or hydrogen peroxide would be likely to provide a hydroperoxide intermediate and only the latter reactions are substantially chemiluminescent. A number of peroxidic compounds have been designed to test the generality of this implied relationship and to examine the relationship of structure to light yield.

The acridines represent a particularly attractive compound group upon which to base the design of new chemiluminescent materials. Many members of the class have the high fluorescence efficiency required for an efficient emitting species in chemiluminescence. Moreover, several reactive acridine derivatives can be readily prepared to serve as versatile starting materials for synthesis. Some approaches and attempts to synthesize potentially chemiluminescent compounds based on acridine chemistry were described in Technical Report No. 1[30].

In the present report we describe work in progress aimed at providing compounds I and II for chemiluminescence testing. In

each case, decomposition would be expected to provide the highly fluorescent N-methylacridanone, while homolysis of peroxidic oxygen bonds would contribute to the required energy. The mechanistic pathways available for decompositions of I and II, however, are clearly and substantially different.


I

II
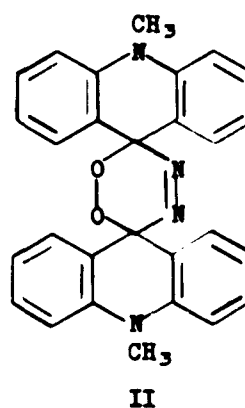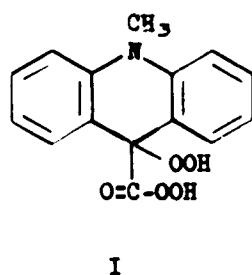
Compound I is being synthesized by the following route:
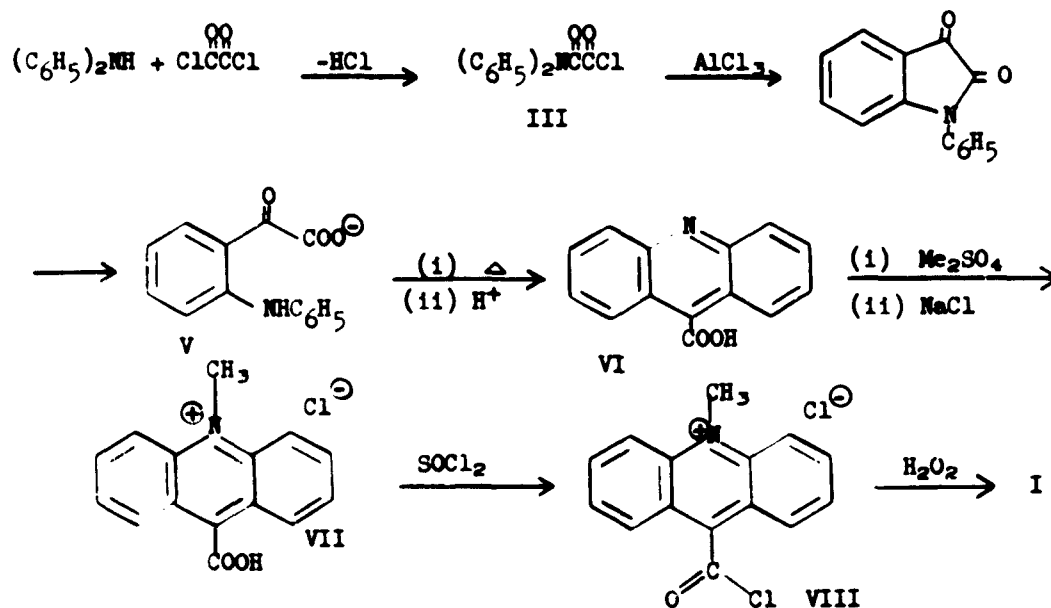
Stolle et al.[31,32] have briefly described the route to VI though without experimental detail. In our hands diphenylamine and oxalyl chloride were readily condensed in refluxing benzene with evolution of hydrogen chloride to afford N,N-diphenyloxamoyl chloride (III) in 80% yield. Aluminum chloride catalyzed ring closure was readily achieved in carbon disulfide to give orange needles of N-phenylisatin (IV) in 60% yield. Ring opening of IV in alkali at the amide link was particularly facile, the product (V) recrystallizing from aqueous ethanol as pale yellow plates which, on drying, lost solvent of crystallization and turned to an intense yellow powder (88% yield). The pyrolysis step advised by Stolle and coworkers[32] has proved disappointing, work-up affording only aprox., 10% of theory of a 1:1 adduct of acridine-9-carboxylic acid (VI) and acetic acid. However, a recent small-scale test of a modification due to Friedlander and Kunz[33] which simply involves heating the ring-opened salt (V) in excess aqueous base appears to obviate this problem and on neutralization affords a high yield of the acridine carboxylic acid. Preliminary experiments to effect methylation of the ring nitrogen in preference to the acid function have been successful. As may be anticipated, the reaction is sluggish, but the acid has been converted in 39% yield to the 9-carboxy-10-methylacridinium chloride (VII) by treatment with excess dimethylsulfate at 90° for three days. It appears that the chlorination of the carboxyl group is also sluggish, no acid chloride being obtained after refluxing VII in excess thionyl

chloride for twelve hours. Extended reaction periods or the use of oxalyl chloride instead of thionyl chloride can be expected to overcome this problem.

Effort in developing a synthetic route to compounds of type II has been confined to a study of preparative methods for the possible autoxidation precursors IX and X. The azine IX was first isolated as
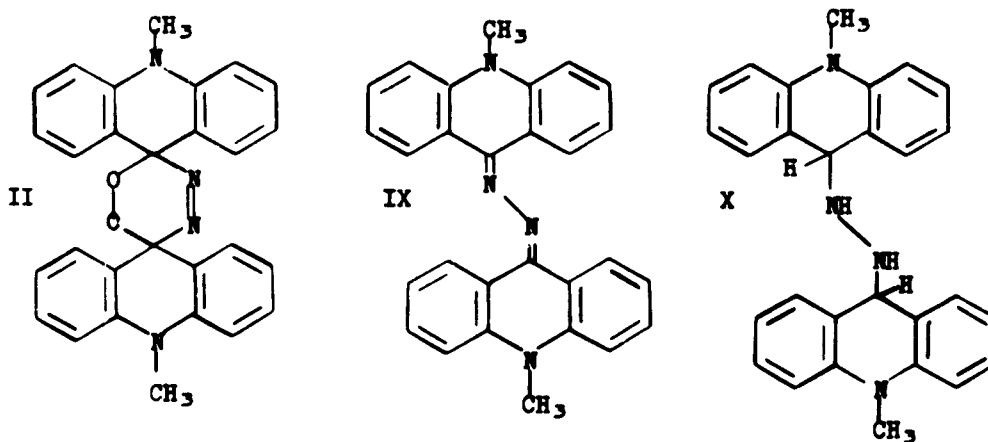
a low yield product from an attempt to prepare the hydrazo compound X by reaction of N-methylacridinium chloride with hydrazine. The major products of the reaction, however, were N-methylacridanone XI and 9,9'-bis-(N-methylacridan), XII.
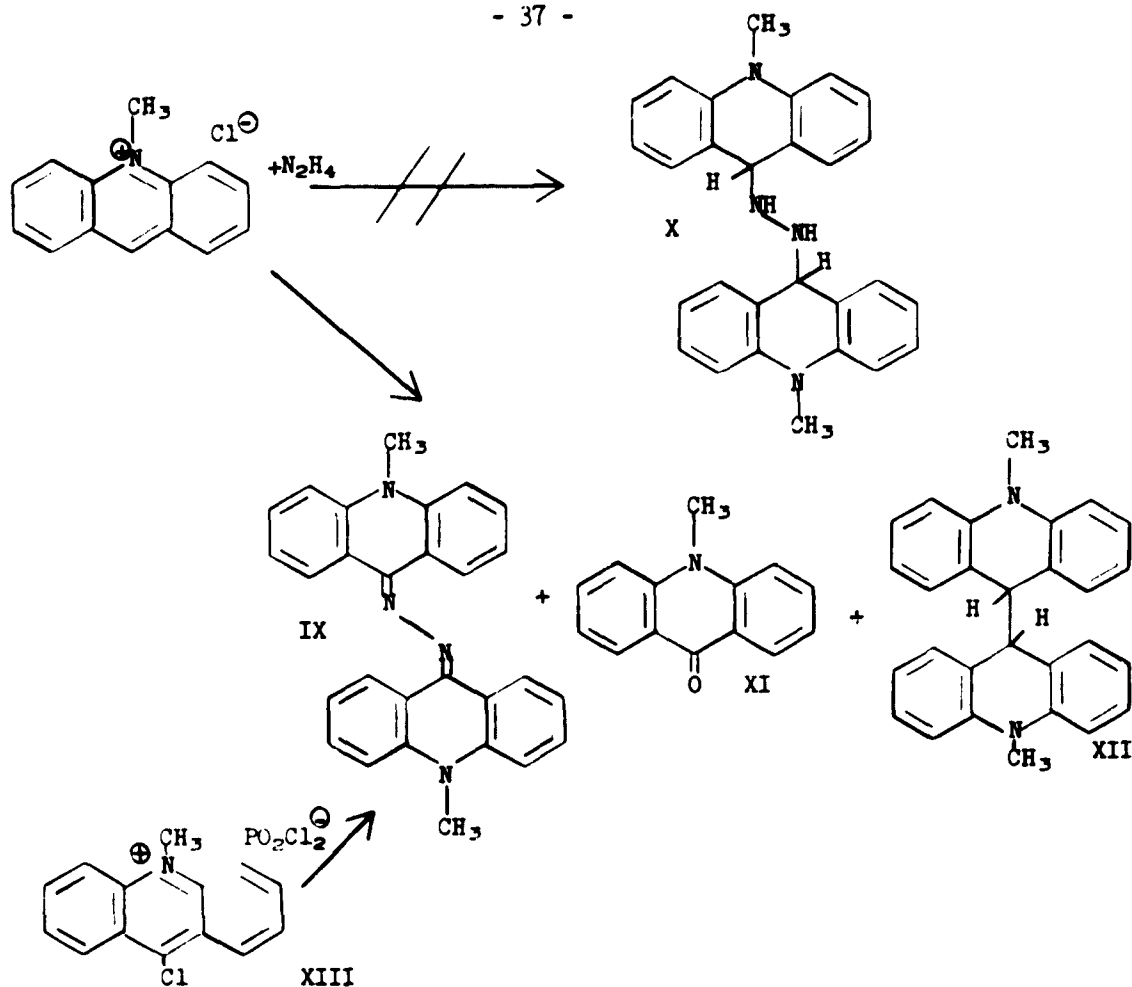
Surprisingly, the reaction of hydrazine with 9-chloro-N-methyl-acridinium dichlorophosphate (XIII) produced the same three products but with IX and XII as the major components of the mixture. Gleu and Scharschmidt[34] have reported that the azine IX is the sole product of this latter reaction under a variety of reaction conditions. Some further study of these reactions is planned in an endeavor to improve the yield of the azine (IX) and also to avoid the tedious separatory

procedures necessary to isolate the product. The major effort, however, will be directed towards a study of the autooxidation of the azine in hand and the similar compound (XIV) described previously[30].

XIV
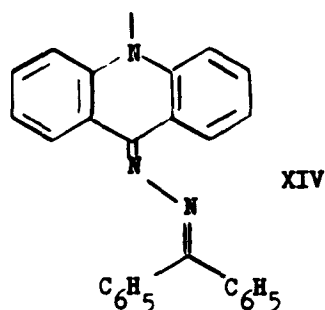
2. 9,10-Azoanthracenes

Additional, but unsuccessful, efforts have been made to prepare azoanthracenes XV and XVI, described in the previous report[2]. As discussed in detail in that report, these materials are wanted so that their potential chemiluminescent properties can be compared with the known chemiluminescence obtained by decomposition of the corresponding photoperoxides XVII and XVIII.

XV   XVI   XVII   XVIII
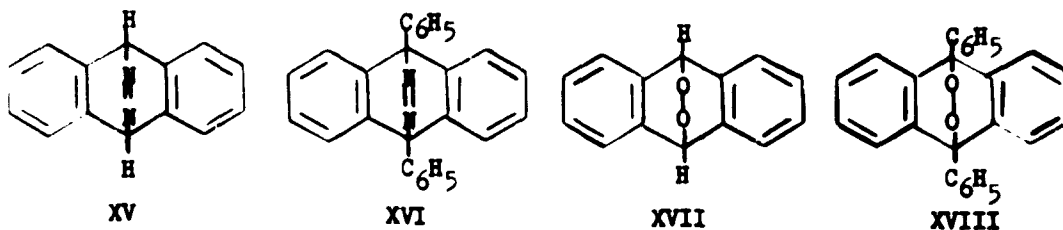
Attempts to hydrolyze the anthracene-diethylazodiformate adduct
XIX with ethanolic sodium hydroxide according to a reported procedure[39]
have not given a product analyzing satisfactorily for the hydrazoanthra-
cene XX needed for preparation of XV.
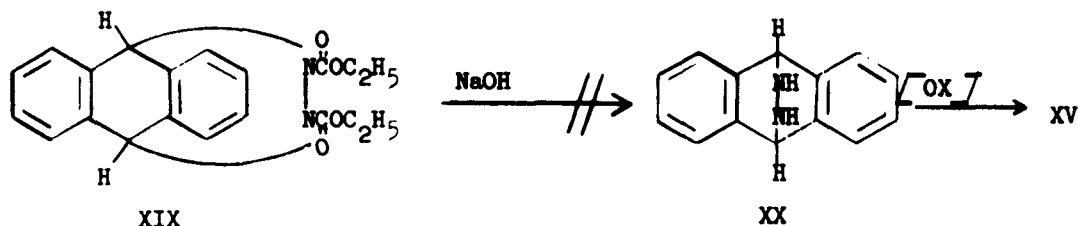
In several experiments an acid-soluble product was obtained having an
infrared spectrum in excellent agreement with that expected for XX, but
more generally the spectrum indicated the presence of a carbonyl contami-
nent. Elemental analysis indicated, however, that the product contained
less than one-half the nitrogen required for XX. Nevertheless, the acid-
soluble hydrolysis product gave anthracene in substantially quantitative
yields when oxidized with mercuric oxide or with hydrogen peroxide or
with Fremy's salt as would be expected for an oxidation of XX proceeding
through the azo compound XV, followed by elemination of nitrogen. These
oxidations were not chemiluminescent. Further efforts to prepare an
unambiguously authentic sample of XX will be suspended.

Attempts to react 9,10-dichloro-9,10-diphenyl-9,10-dihydro-
anthracene XXI, with hydrazine or with alkaline diethylhydrazodicarboxyl-
ate, under a variety of conditions have failed to give hydrazines XXII
or XXIII needed for preparation of XVI.
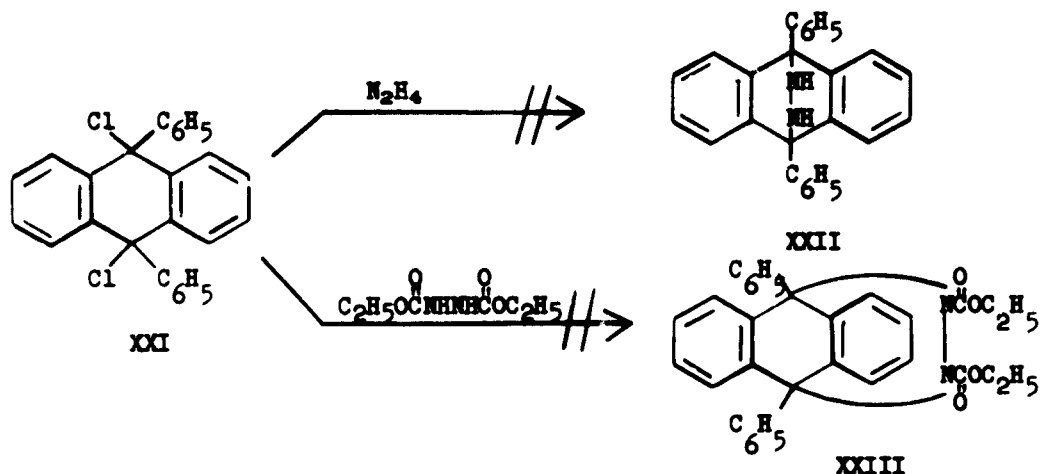
The dichloroanthracene XXI is reported to react normally with aniline to give the 9,10-dianilino adduct, and to react only slowly with water[36]. However, reaction of XXI with hydrazine in a mixture of chloroform and aqueous sodium bicarbonate unexpectedly gave a nitrogen-free compound, analyzing for $C_{32}H_{32}O_2$.

Reaction of XXI with hydrazine in anhydrous dimethylformamide has also failed to give XXII. An effort will be made to achieve the reaction under other conditions.

Reactions of XXI with diethylhydrazodiformate and potassium tert.-butoxide in tert. butyl alcohol or dimethylformamide at room temperature did not proceed to give hydrazine XXIII. Unchanged starting material was recovered from the former reaction; under the latter conditions a mixture of products was obtained from which XXIII could not be isolated. In view of these unsatisfactory preliminary results and the probable difficult hydrolysis of XXIII to XXII, this approach is being discontinued.

B. Highly Fluorescent Phthalhydrazides

A continuing effect to prepare 2,3-dihydropyradazino $[$ 4,5-c $]$ acridine-1,4,7-(12H)trione (XXIV), described in the previous reports,[2,30] has been successfully completed.
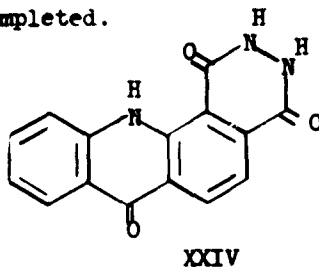
XXIV

As discussed in the first report[30], a highly fluorescent emitting species is essential for good chemiluminescence efficiency. Compound XXIV was designed to test the possibility that the chemiluminescence common to phthalhydrazide oxidation might be substantially improved by specifically providing for the formation of a highly fluorescent emitter. While fluorescence efficiency is difficult to forecast, the emitter produced by oxidation of XXIV would necessarily incorporate the highly fluorescent acridone backbone and thus be likely to have good fluorescence.

The preparation of XXIV was completed by the following steps.
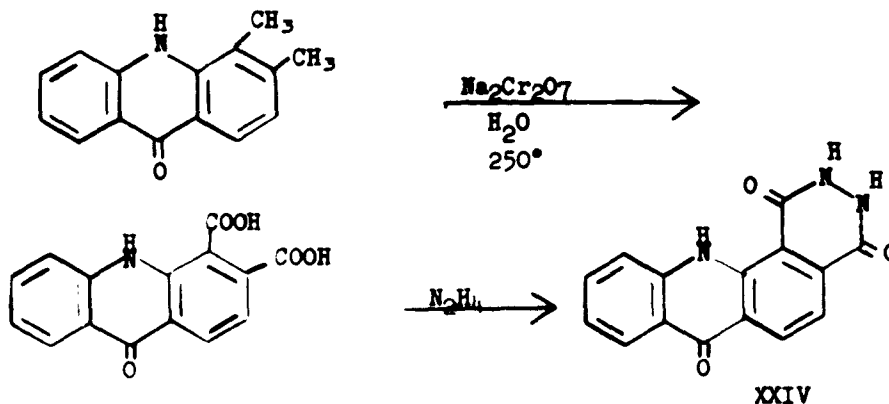
Oxidation of 3,4-dimethylacridone by sodium dichromate gave 3,4-di-

carboxyacridone in 30% yield, and reaction of the acid with hydrazine provided the phthalhydrazide XXIV in 54% yield.

Preliminary chemiluminescence tests of phthalhydrazide, XXIV, with aqueous alkaline hydrogen peroxide and hemin or with oxygen in alkaline dimethylsulfoxide were encouraging with moderate intensities and lifetimes being observed. However, quantitative measurement of the chemiluminescence quantum yield for the reaction with aqueous alkaline hydrogen peroxide and potassium persulfate indicated an efficiency of only about 0.1%. While this efficiency places XXIV among the most efficient chemiluminescent materials, it is an order of magnitude less than the 1% yield[2] measured for 3-aminophthalhydrazide under the same conditions.

As a measure of the fluorescence efficiency of the emitting species from oxidation of XXIV, the fluorescence quantum yield of 3,4-dicarboxyacridone dianion was determined in 0.1 $\underline{M}$ sodium carbonate solution. The quantum yield value obtained was 13%, far less than hoped for but still substantially higher than the 8% fluorescence quantum yield reported for 3-aminophthalate dianion[37], the corresponding oxidation product and suspected emitter from 3-aminophthalhydrazide.

The failure of chemiluminescence efficiency to increase with increasing fluorescence efficiency indicates that the effect of structural change on the yield of electronically excited molecules outweighs the importance of fluorescence efficiency in the phthalhydrazide series. This approach, which might have provided a quick solution to practical chemiluminescence thus appears unworkable in the phthalhydrazide series.

C. Polymeric Luminants

Practical application of chemiluminescence to area lighting will require a system that retains its efficiency at relatively high luminant concentrations. Achievement of this requirement is complicated by fluorescence quenching, a well-known process by which electronic energy is converted non-radiatively to heat during collision of excited molecules with starting materials, reaction by-products or the corresponding ground state molecules. Adverse concentration effects have been observed in a number of chemiluminescent systems including the 3-amino-phthalhydrazide reaction, where efficiency loss begins at about 10^{-3} molar. Since fluorescence quenching is a collisional process, efficiency loss might be reduced by incorporating the luminant structure in a relatively immobile polymer backbone[30]. Since quenching occurs generally at every collision, and the lifetimes of singlet excited states are short (10^{-7} to 10^{-8} seconds), even a small decrease in collision frequency would increase emission efficiency.

As a test of this approach we have attempted to prepare the polyamide XXIV and the polyurea XXX by the following routes.

XXV + ClCYCCl $\xrightarrow{\hspace{2cm}}$ XXVII $\xrightarrow{N_2H_4}$

XXVI

XVIII

XXV + $\xrightarrow{\hspace{2cm}}$ XXIX

$\xrightarrow{N_2H_4}$ XXX
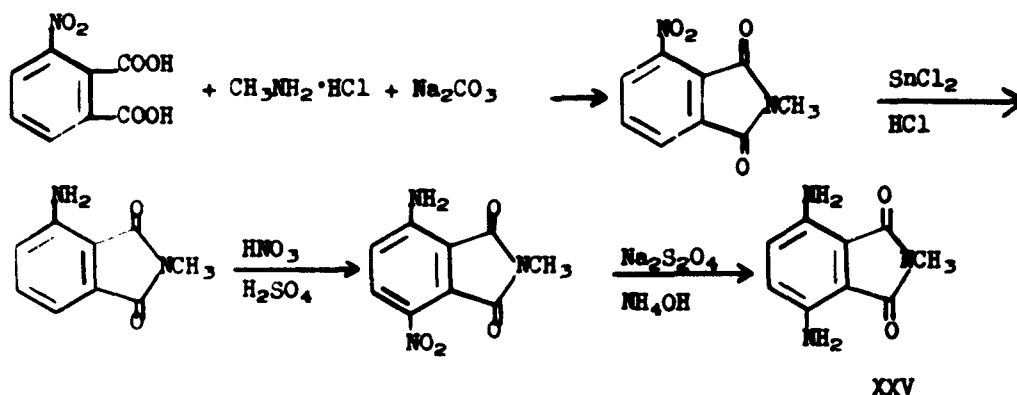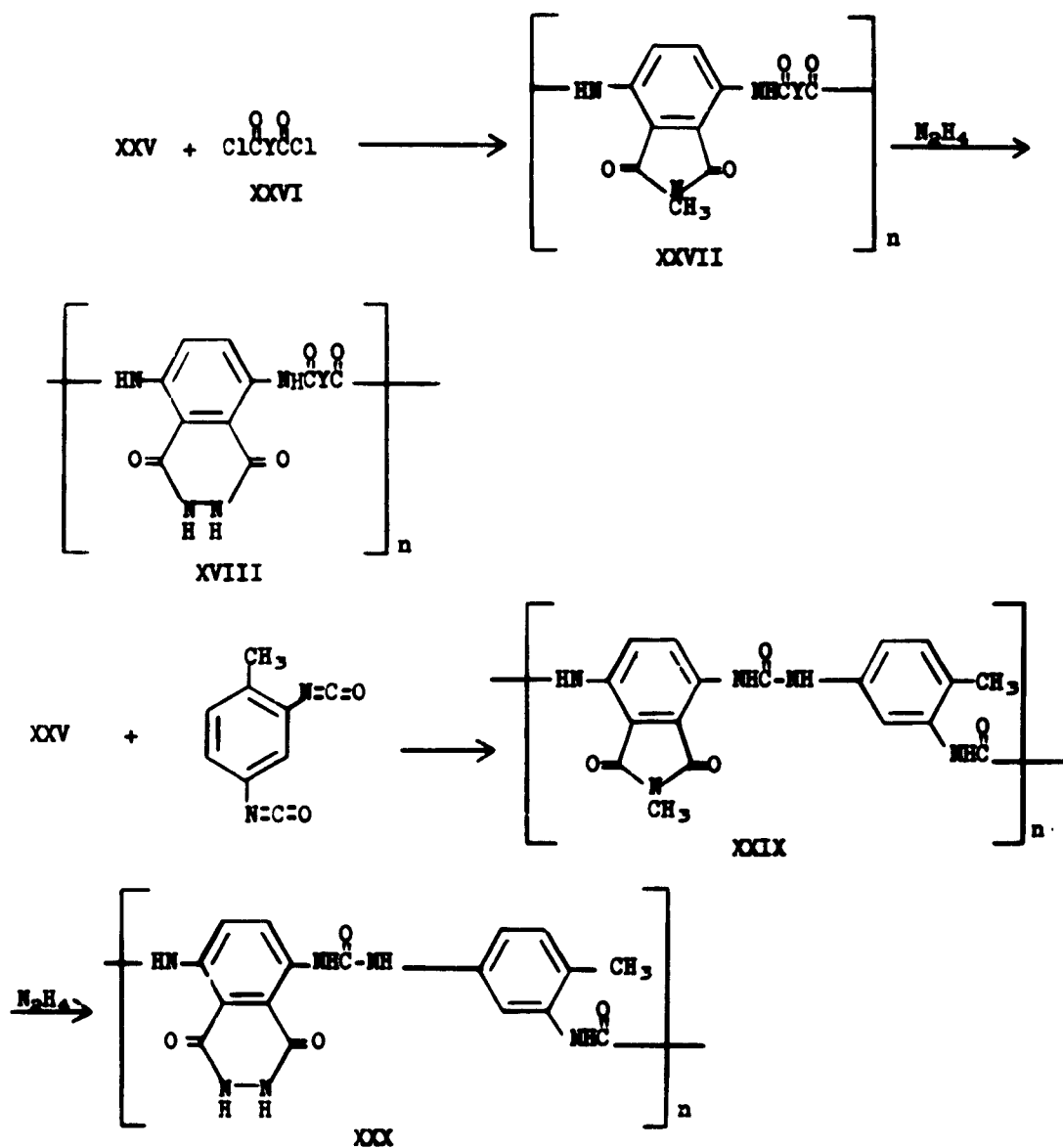
Reaction of diamine XXV with sebacyl chloride (XXVI, Y = -(CH$_2$)$_8$-) or terphthaloyl chloride (XXVI, Y =) by the interfacial polymerization method failed to give high molecular weight products corresponding

to XXVII[2]. Reaction of XXV with toluene diisocyanate, however, gave a product having the properties expected for the polyurea XXIX[2]. Reaction of XXIX with hydrazine in dimethylformamide has now provided the polymeric hydrazide XXX, characterized by its infrared spectrum, base solubility, and positive chemiluminescence tests with alkaline hydrogen peroxide and hemin or potassium persulfate.

Reaction of XXX with excess hydrogen peroxide and potassium persulfate in aqueous sodium carbonate solution was found to generate a bright flash followed by a dim but exceptionally long-lived emission. The flash probably resulted from rapid reaction of a low molecular weight constituent of the polymeric material. Quantitative intensity measurements of the emission at three luminant concentrations (See Section III) are summarized in the following chart:

Luminant Conc. Moles per Liter	Concentration Ratio	Relative Intensity		
		2 Min.	10 Min.	18 Min.
4×10^{-3}	1	1	0.9	0.9
3×10^{-2}	7.5	2.2	1.6	1.6
1×10^{-1}	25	4.2	-	-

It is clear from the results that the polyurea provides little relief from efficiency loss at high concentration. Unfortunately, the significance of the experiment was obscured by the rapid development of a dark color in these reactions even at low concentration. Since the opaqueness increased markedly with increasing concentration, loss of efficiency may have been caused by increasing absorption rather than by true quenching. An unambiguous answer will require a polymeric luminant producing non-absorbing products.

SECTION II

EXPERIMENTAL

N,N-Diphenyloxamoyl Chloride (III). In a three-necked, 500-ml. flask equipped with a stirrer, addition funnel and condenser, 42 g. (0.25 mole) of diphenylamine was dissolved in 200 ml. of benzene. The rapid addition of 32 g. (0.25 mole) of oxalyl chloride caused a mild exotherm (25-50°) and a white solid precipitated. The mixture was refluxed for three hours, during which time the precipitate redissolved. After standing overnight half of the benzene was evaporated on the steam bath and 250 ml. of boiling heptane was added. The solution remained clear and on cooling the product crystallized, was collected and dried to afford 50 g. (80%) of N,N-diphenyloxamoyl chloride, m.p. 73-74° (lit. 70°[32]).

Anal: Calc'd. for $C_{14}H_{10}NO_2Cl$: C, 64.8; H, 3.86; N, 5.4; Cl, 13.7.

Found: C, 64.8; H, 3.73; N, 5.6; Cl, 13.7.

N-Phenylisatin (IV). A solution of 50 g. (0.193 mole) of N,N-diphenyloxamoyl chloride in 250 ml. of carbon disulfide was added dropwise during 10 min. to a suspension of 33.5 g. (0.25 mole) of aluminum chloride in 300 ml. of carbon disulfide in a three-necked, one liter flask fitted with an addition funnel, stirrer and condenser. A black precipitate developed and the mixture was refluxed for 1 hour. The carbon disulfide was decanted, discarded and replaced by 500 ml. of ice-water. On agitation the black solid slowly turned orange. Filtration and recrystallization from 250 ml. of 95% ethanol afforded 26 g. (60%) of N-phenylisatin as orange needles, m.p. 140-141° (lit. 138°[32]).

Anal: Calc'd. for $C_{14}H_9NO_2$: C, 75.3; H, 4.04.

Found: C, 75.0; H, 4.07.

Acridine-9-carboxylic Acid (VI). In a 100-ml. Erlenmeyer flask 6 g. of N-phenylisatin was combined with a solution of 20 ml. of ethanol and 40 ml. of 2N aqueous sodium hydroxide. The orange solid immediately turned yellow. The mixture was warmed to obtain a clear solution and the hydrolysis product (V) crystallized on cooling as pale yellow plates. On drying the product lost solvent of crystallization and became deep yellow affording 6.2 g. (88%) of the salt (V) m.p. 245° dec. This product was heated at 250° for 30 min. cooled and dissolved in 200 ml. of water. The solution was acidified and the resulting precipitate filtered and recrystallized from acetic acid to afford

0.5 g. of a 1:1 adduct of acridine-9-carboxylic acid (VI) and acetic acid as indicated by infrared and microanalysis.

Anal: Calc'd. for $C_{14}H_9NO_2 \cdot C_2H_4O_2$: C, 67.9; H, 4.60; N, 5.0.

Found: C, 68.2; H, 4.62; N, 5.2.

9-Carboxy-10-methylacridinium Chloride (VII). A solution of 2.4 g. of acridine-9-carboxylic acid-acetic acid adduct in 25 ml. of dimethyl sulfate was contained in 50-ml. flask fitted with a condenser and drying tube and heated on a steam bath for 3 days. The mixture was poured into 200 ml. of ether and extracted with two 200-ml. portions of water. The separated aqueous extract was filtered, warmed and saturated with sodium chloride. On cooling long yellow needles of the acridinium salt (VII) crystallized. Filtration, drying and sublimation in vacuo afforded 0.9 g. (39%) of material, m.p. 270° dec.

Anal: Calc'd. for $C_{15}H_{12}NO_2Cl$: C, 65.9; H, 4.42; N, 5.1; Cl, 12.9.

Found: C, 65.0; H, 4.48; N, 5.1; Cl, 12.7.

Reaction of Hydrazine and N-Methylacridinium Chloride. In a 500-ml., three-necked flask fitted with an addition funnel, stirrer and condenser, 26.5 g. (0.1 mole) of N-methylacridinium chloride was dissolved in 200 ml. of hot 95% ethanol. A solution of 2.5 ml.(0.05 mole) of hydrazine hydrate and 10 ml. (0.1 mole) of triethylamine in 50 ml. of ethanol was added dropwise during 15 min., and the mixture refluxed for three hours. A brick-red precipitate was filtered from the hot mixture and the filtrate, on cooling, afforded long mauve needles. The latter (2.2 g.) was filtered, recrystallized from ethanol and shown by infrared and n.m.r. analysis to be N-methylacridan-9-one (XI), m.p. 202-204°.

The brick-red solid (7.2 g.) filtered from the hot reaction mixture was dissolved in hot chloroform and cooled to afford 4 g. of 9,9'-bis(N-methylacridan), XII, m.p. 240-260° dec. (Lit.[38] ca. 280° dec.)

Anal: Calc'd for $C_{28}H_{24}N_2$: C, 86.5; H, 6.23; N, 7.2.

Found: C, 86.2; H, 6.41; N, 7.5.

The filtrate from this last recrystallization was evaporated to half its volume and some hot ethanol was added causing 150 mg. of the deep red azine (IX), m.p. 290-295°, to crystallize.

Anal: Calc'd. for $C_{28}H_{22}N_4$: C, 81.1; H, 5.37; N, 13.7.

Found: C, 81.1; H, 5.06; N, 13.5.

Further evaporation of the final filtrate and cooling afforded
an additional 1.2 g. of the bis-acridan (XII).

Reaction of Hydrazine with 9-Chloro-10-methylacridinium Dichlorophosphate.

When a freshly prepared solution of the above
acridinium salt (5 g.) in ice-water was mixed with 275 ml. of 10%
aqueous hydrazine solution in a 500-ml. Erlenmeyer flask, a brick-red
solid immediately precipitated and was filtered. Trituration with
methanol (150 ml.) and filtration left a red solid which was predomi-
nantly the azine (IX) as shown by infrared analysis. Repeated recrystal-
lization from anisole afforded the pure azine. The methanol extract on
evaporation afforded a yellow solid which was shown by infrared analysis
to be predominantly the bis-(N-methylacridan), XII, contaminated with
the azine (IX) and N-methylacridanone (XI). Again repeated recrystal-
lization from anisole afforded a pure sample of the dimer, XII.

Anthracene Biimine (XX).

A hot solution of 10 g. (0.028 mole)
of diethylazodiformate-anthracene adduct, XIX, in 50 ml. of absolute
ethanol was added to a cooled (0°) solution of sodium ethoxide prepared
from 8.5 g. (0.37 g. atoms) of sodium metal and 200 ml. of absolute
ethanol. Six ml. of distilled water was added at once. A nitrogen
atmosphere was maintained throughout. The mixture then stood at room
temperature under nitrogen for 20 hours. An additional 10 ml. of
distilled water (containing a trace of ethylenediaminetetraacetic acid)
was added. A rotary evaporator was used to remove the ethanol at 30-35°,
and the residual solid was taken up in a mixture of 100 ml. of distilled
water and 100 g. of ice made from distilled water. This mixture was
acidified with 10% hydrochloric acid, using dry ice to maintain low
temperature. After filtration, the cooled filtrate was made basic with
5% sodium hydroxide. The resulting precipitate was collected in three
crops to yield 2.58 g. (44%) of product. The infrared spectrum was in
excellent agreement with that expected for anthracene biimine except
for some contamination of the desired product with a carbonyl contain-
ing compound, possibly the half-hydrolyzed starting material. The
product decomposed at 130° (Lit.[39] decomposition pt. 100°).

Anal: Calc'd. for $C_{14}H_{12}N_2$: C, 80.74; H, 5.92; N, 13.45.

Found: C, 74.93; H, 5.38; N, 5.06.

Two repetitions of this procedure gave similar results.
This product was used in reactions with mercuric oxide in benzene at
10°, with hydrogen peroxide in acetone at 10°, and with Fremy's salt,
$ON(SO_3K)_2$, in 5% acetic acid at 0°, in attempts to obtain the azo-
anthracene by oxidation. In all three experiments anthracene was the
only isolable product. In the Fremy salt reaction 51% of the theo-
retical yield of anthracene was recovered. The other reactions gave
quantitative yields of anthracene. None of the oxidation reactions
were chemiluminescent.

Attempted Preparation of 9,10-Diphenylanthracene Biimine (XXII).
A. To a stirred solution of 2 g. (0.005 mole) of 9,10-diphenyl-9,10-
dichloro-9,10-dihydroanthracene in 75 ml. of chloroform at 5° was added
over a period of 15 seconds 0.25 g. (0.005 mole) of cold 64% aqueous
hydrazine. The reaction mixture was stirred 4 hours at 5°. The organic
phase was separated and the solvent was dried and evaporated under
reduced pressure. The residue was collected, dissolved in benzene, and
chromatographed on neutral alumina. Two distinct materials were obtained.
The first product, m.p. 195°, appeared from its infrared spectrum to be
an ether (empirical formula: $C_{32}H_{32}O_2$).

Anal: Found: C, 85.18; H, 6.96; O, 6.92.

The second product from the chromatographic column, m.p. 185-
205°, found in trace amounts, appeared from its infrared spectrum to be
a phenone. Nitrogen containing products were not found.

B. To a solution of 3 g. (0.0075 mole) of 9,10-diphenyl-9,10-
dichloro-9,10-dihydroanthracene in 100 ml. dry dimethylformamide was
added with stirring at room temperature a solution of 0.38 g. (0.0075
mole) of anhydrous hydrazine in 100 ml. dry dimethylformamide. The
mixture was stirred 6 hrs. at room temperature, and then diluted with
1 ℓ of water. A pale yellow precipitate settled out of solution, and
was collected and dried. The infrared spectrum and the elemental
analysis indicated that the material was not the desired product. The
empirical formula calculated was $C_{30}H_{25}NO_2$. The material was not
characterized further.

Anal: Calc'd. for $C_{26}H_{20}N_2$: C, 86.65; H. 5.60; N, 7.77.

Found: C, 83.62; H, 5.86; N, 3.25; O, 6.80.

Attempted Preparation of the Diethylazodiformate Adduct with
9,10-Diphenylanthracene (XXIII). A. To a stirred mixture of 2 g. (0.005
mole) of 9,10-diphenyl-9,10-dichloro-9,10-dihydroanthracene and 50 ml.
of t-butanol was added at room temperature 1.1 g. (0.01 mole) of
potassium t-butoxide and 0.9 g. (0.005 mole) of diethylhydrazodi-
carboxylate. The reaction mixture was stirred 16 hrs. at room tempera-
ture. One third of the solvent was evaporated under reduced pressure,
and the residue was diluted with 5 volumes of water. Unchanged 9,10-
dichloro-9,10-diphenyl-9,10-dihydroanthracene (1.5 g., 75%) separated.
Other products were not found.

B. The preceding reaction was carried out using dry
dimethylformamide as solvent with a reaction time of 48 hrs.

The reaction mixture was filtered, and the filtrate was
diluted with 10 volumes of water. A pale yellow solid precipitated,
and was collected, washed well with water, and dried.

A portion of the product was crystallized from a mixture of
ethanol and water to obtain a small yield of 9,10-diphenylanthracene.

A second portion of the product was dissolved in ether and
crystallized at -70°. A small yield of solid was separated and was
shown by infrared analysis and melting point to be anthraquinone.

Nitrogen-containing products were not found.

3,4-Dicarboxyacridone. An autoclave was charged with 5 g.
(0.026 moles) of 3,4-dimethylacridone, 15.1 g. (0.052 moles) of sodium
dichromate and 100 ml. of water. The autoclave was heated rapidly to
250°, held at 250° for one hour and then cooled rapidly. The solution
was filtered and the filtrate was decolorized by heating with activated
charcoal. Acidification with 6 N sulfuric acid precipitated a fluor-
escent yellow solid. Recrystallization from dilute acetic acid gave
2.3 g. (31%) of material, m.p. 250° dec.

Anal: Calc'd. for $C_{15}H_9NO_5$: C, 63.63; H, 3.20; N, 4.94;
O, 28.25.
Found: C, 63.46; H, 3.80; N, 4.95; O, 28.25.

2,3-Dihydropyradazino/4,5-c/acridine-1,4,7 (12H)trione(XXIV).
A mixture of 1.5 g. (0.0053 moles) 3,4-dicarboxyacridone in 3 ml. of 8%
hydrazine solution and 4 ml. triethylene glycol was gradually heated with
a bunsen burner to 215° and maintained at 215° until the solution turned
red (about 3 minutes). On cooling a mustard-yellow solid formed. The
solid was collected, washed with water, and dried to yield 0.812 g.
(54%) product, m.p. dec. >230°.

This hydrazide was tested for chemiluminescence under several
conditions. In alkaline dimethylsulfoxide with oxygen a moderate amount
of light was obtained. In a basic aqueous solution with 30% hydrogen
peroxide the hydrazide produced a weak light which became much brighter
when a few crystals of hemin were added. Results obtained in a series
of qualitative tests with aqueous alkaline potassium persulfate and
hydrogen peroxide are summarized in the following chart.

Anal: Calc'd. for $C_{15}H_9N_3O_3$: C, 64.50; H, 3.24; N, 15.05.

Found: C, 61.90; H, 3.68; N, 15.02.

Chemiluminescence Tests in Aqueous Solution

	Acridone Hydrazide (Molarity)	Potassium Persulfate (Molarity)	Hydrogen Peroxide (Molarity)	Base (Na$_2$CO$_3$ Molarity)	Light Intensity
1)	1×10^{-3}	1×10^{-2}	3×10^{-2}	1×10^{-3}	weak
2)	1×10^{-3}	1×10^{-1}	$3 \times 10^{-2*}$	1×10^{-3}	medium
3)	1×10^{-3}	6×10^{-2}	3×10^{-2}	1×10^{-3}	weak
4)	1×10^{-3}	6×10^{-2}	3×10^{-2}	5×10^{-3}	weak
5)	1×10^{-3}	6×10^{-2}	3×10^{-2}	(NaOH) 1×10^{-2}	weak
6)	1×10^{-3}	6×10^{-2}	3×10^{-2}	5×10^{-2}	weak
7)	1×10^{-3}	6×10^{-2}	3×10^{-1}	(NaOH) 1×10^{-1}	weak
8)	1×10^{-3}	6×10^{-2}	3×10^{-1}	1×10^{-3}	weak

* Following the intensity observation the peroxide concentration was gradually increased up to 8×10^{-2} but no further improvement resulted.

Reaction of Hydrazine and Diethylazodiformate-Anthracene Adduct.

The adduct of anthracene and diethylazodicarboxylate 5 g. (0.014 mole) was refluxed with 3.3 g. (0.056 mole) aqueous hydrazine in 100 ml. 2B ethanol for seventy-two hours. After cooling and filtration 4.55 g. (90%) of the starting adduct was recovered.

Similar experiments carried out in refluxing ethylcellosolve for four hours and refluxing dimethylformamide also resulted in recovery of unchanged starting material.

In a third experiment an autoclave was charged with 5 g. (0.014 mole) of the anthracene adduct, 30 ml. of 64% aqueous hydrazine and 60 ml. of dimethylformamide. The autoclave was heated rapidly to 250°, held at 250° for one hour and cooled rapidly. Collection of the solid product yielded 1.74 g. of anthracene. Dilution and acidification of the filtrate gave a small amount of anthracene. Other products were not found.

Preparation of Phthalhydrazide Polyurea Copolymer (XXX). To
a solution of 5 g. of phthalimide polyurea copolymer, XXIV, (prepared
from 3,6-diamino-N-methylphthalimide and toluene, 1,4-diisocyanate[2])
in 50 ml. of dry dimethylformamide was added 5 g. (0.1 mole) of 64%
aqueous hydrazine. The reaction mixture was refluxed 10 hrs., then
filtered. A gray solid was collected. The filtrate was diluted with
25 volumes of water. A small amount of yellow material precipitated
and was collected. The products were combined and dissolved in 5%
sodium hydroxide, treated with activated charcoal, then precipitated
with 10% hydrochloric acid. The gelatinous precipitate was collected
by centrifuging and solidified by treatment with acetone to obtain
0.6 g. (12%) of material, m.p. 300°. Infrared analysis was
compatible with the expected copolymer, and a base-peroxide aqueous
chemiluminescence test was positive.

SECTION III

SPECTROSCOPY AND ENERGY TRANSFER

A. Oxalyl Chloride-Hydrogen Peroxide Chemiluminescence

As discussed in Section IA, a critical aspect of the chemi-
luminescent reaction between oxalyl chloride and hydrogen peroxide in
the presence of a fluorescent compound is the mechanism of the process
by which chemical energy released in the reaction of oxalyl chloride
with hydrogen peroxide appears as electronic excitation energy in the
fluorescent compound. A spectroscopic program is in progress to
examine the transfer process in detail. The initial results are
summarized below.

The Emitting Species

Normalized fluorescence spectra of 9,10-diphenylanthracene
and pyrene are compared with the spectra of the corresponding chemi-
luminescent reactions in Figures I, II and III. The close correspond-
ance between chemiluminescence and fluorescence spectra obtained with
each acceptor leaves little doubt that the excited singlet state of the
acceptor is the emitting species in the chemiluminescent systems. The
loss of the 410 mu 9,10-diphenylanthracene band in the chemiluminescence
spectrum of Figure II results from reabsorption by 9,10-diphenylanthracene
at the relatively high concentration used. Reabsorption is not observed
in the corresponding fluorescence measurement, since front-side
illumination is used and the fluorescence emission does not traverse
the bulk of the solution.

Fluorescence measurements carried out immediately after the chemiluminescent reaction with 9,10-diphenylanthracene were similar with respect to both distribution and intensity to measurements made prior to reaction, demonstrating that 9,10-diphenylanthracene is not consumed in the reaction to any appreciable extent. The stability of 9,10-diphenylanthracene under the chemiluminescent reaction conditions is further demonstrated by the UV absorption curves in Figure IV. The absorption spectrum is seen to be essentially unchanged following the reaction.

Effect of Acceptor Concentration

The fluorescence spectrum and quantum yield of 9,10-diphenyl-anthracence have been measured as a function of concentration from 6×10^{-6} molar to 2×10^{-2} molar in ether containing hydrogen peroxide. With front-side illumination the spectral distribution was unchanged throughout the concentration range studied showing that self-absorption is negligible under these conditions. The fluorescence quantum yield, however, was found unexpectedly to increase from 0.54 to 0.84 with increasing 9,10-diphenylanthracene concentration as indicated in Table I. This result will be studied further. As expected, the efficiency remains constant at 0.84 in the absence of hydrogen peroxide. The effect of oxalyl chloride on the fluorescence quantum yield of 9,10-diphenyl-anthracene will be determined in the near future.

The observed chemiluminescence spectral distribution does change with increasing 9,10-diphenylanthracene concentration. It can

be shown, however, that the observed spectral change results from self-absorbtion, since in chemiluminescence the emission occurs from the entire depth of solution. The chemiluminescence quantum yield increases markedly with increasing 9,10-diphenylanthracene concentration up to a limiting value of about 2% under the conditions studied as indicated in Table II. This is the anticipated result, and indicates that the acceptor traps energy by a collisional process from an unstable species which by itself would lose its energy as heat.

Distribution of Chemiluminescence Between Two Acceptors

It can be shown that collisional energy transfer from a primary excited state to two acceptors will be distributed between the two acceptors according to the following equation:

$$(1) \quad \frac{Ta}{Tp} = \frac{k_a [A]}{k_p [P]}$$

In this equation Ta and Tp represent the fractions of total primary excited state energy transferred to acceptors a and b, respectively, k_a and k_p are collisional transfer rate constants, and $[A]$ and $[P]$ are the concentrations of the two acceptors. It is also evident that the chemiluminescence quantum yield arising from an acceptor will be a function of the chemical yield of the primary excited state, the portion of primary excited state energy transferred to the acceptor and the fluorescence yield of the acceptor as indicated below:

$$(2) \quad Q.Y._a = Y_d \cdot T_a \cdot F_a$$

In this equation $Q.Y._a$ is the chemiluminescence yield arising from acceptor a, Y_d is the chemical yield of the primary (donor) excited state, and F_a is the fluorescence yield of the acceptor. Thus where two acceptors are present, the following relationships apply:

$$(3) \quad \frac{Q.Y._a}{Q.Y._p} = \frac{Y_d \cdot T_a \cdot F_a}{Y_d \cdot T_p \cdot F_p}$$

$$(4) \quad \frac{Q.Y._a}{Q.Y._p} = \frac{k_a \underline{/ A \underline{/}}}{k_p \underline{/ P \underline{/}}} \cdot \frac{F_a}{F_p}$$

It appears from equation (4) that a plot of $\frac{Q.Y._a}{Q.Y._p}$ vs. $\frac{\underline{/ A \underline{/}}}{\underline{/ P \underline{/}}}$ should give a straight line with intercept zero and slope $\frac{F_a}{F_p} \cdot \frac{k_a}{k_p}$. Since F_a and F_p can be determined by independent fluorescence yield measurements, such a plot would permit an estimate of the ratio of the transfer rate constants to the two acceptors.

Transfer rate constant ratios have substantial theoretical significance, since they permit analysis of criteria for efficient transfer to an acceptor. One might expect, for transfer of singlet energy, that transfer efficiency would be dependent on the singlet energy level of the acceptor, increasing as the singlet energy level decreases. Alternatively, if the collisional transfer rates are diffusion controlled, the transfer constant ratios would be unity.

It is necessary in designing a valid experiment for transfer efficiency analysis to avoid the possibility of secondary collisional

transfer from acceptor p to acceptor a. Secondary transfer would give
erroneously high transfer ratios. To avoid this problem, we have chosen
the mixed acceptor system 9,10-diphenylanthracene and pyrene. The
singlet level of 9,10-diphenylanthracene lies below that of pyrene and
thus secondary transfer from pyrene to 9,10-diphenylanthracene might be
expected. However, excited pyrene reacts on collision with ground state
pyrene to form a fluorescence eximer having a singlet state energy level
below that of 9,10-diphenylanthracene[40,41]. Moreover, there is no
ground state molecule corresponding to the eximer[40]. Thus in the
designed experiments excited pyrene is trapped by ground state pyrene
present in large concentration and is substantially restricted from
transfer to the 9,10-diphenylanthracene which is present in much smaller
concentration. Similarly, there is present no ground state molecule of
lower singlet energy than 9,10-diphenylanthracene to act as a quencher.
Since the pyrene eximer is fluorescent, the eximer fluorescence serves
to detect the monomeric pyrene excited state. The energy relationship
is indicated in the following diagram.

S^* ___ $(10^{-6}$ sec.$)$

$(5 \times 10^9$ sec.$^{-1})$

$(10^{-7}$ sec.$)$ S*S

Fl.

3700A

4750A

G

S^*

Fl.

4100A

G

pyrene

9,10-diphenylanthracene
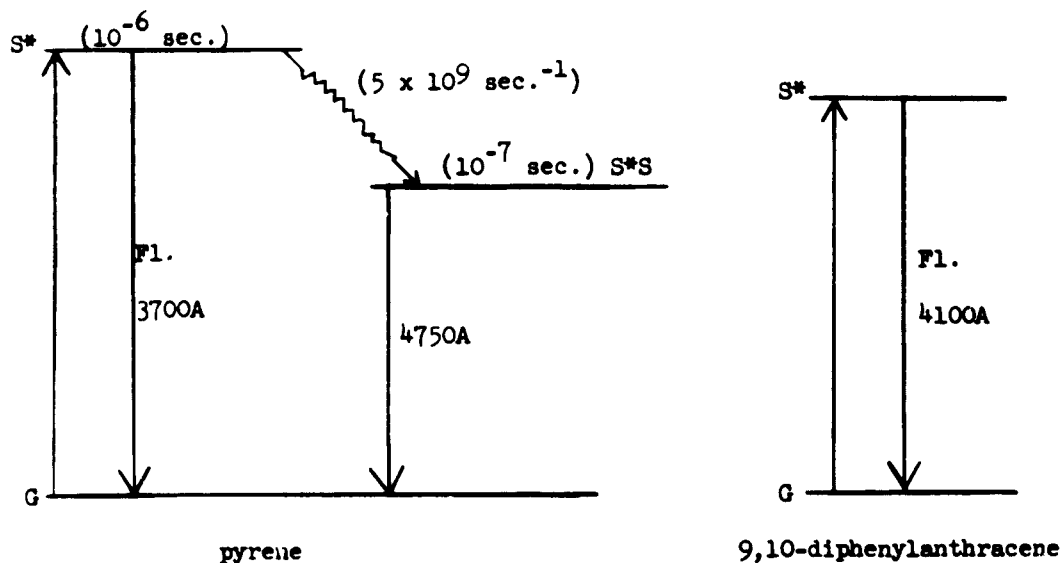
Values in parenthesis are taken from reference 40 and refer to deoxygenated ethanol solutions. The lifetimes of the electronic states involved are expected to be shorter for the experiments performed here.

Initial results from oxalyl chloride-hydrogen peroxide experiments carried out in the presence of both 9,10-diphenylanthracene and pyrene and summarized in Table II. It is seen that the pyrene, present in large excess, captures an approximately constant amount of the available excitation energy. The low values of the pyrene quantum yields reflect the low fluorescence efficiency of the pyrene dimer (Table I). As the 9,10-diphenylanthracene concentration is increased, it captures a progressively greater amount of excitation energy. Even at the

highest concentration studied, however, the 9,10-diphenylanthracene quantum yield is less than one-tenth of that obtained in the absence of pyrene. It is clear that pyrene is the principal acceptor in all the experiments. Typical chemiluminescence spectral curves are shown in Figure 5. Application of the data to equation (4) will be carried out following the determination of fluorescence quantum yields for 9,10-diphenylanthracene and pyrene under the experimental conditions.

The effect of benzophenone, a non-fluorescence energy acceptor, on 9,10-diphenylanthracene emission is indicated in Table II. It is seen that the 9,10-diphenylanthracene quantum yield is substantially higher in the presence of benzophenone than in the corresponding experiment with pyrene. Secondary transfer from benzophenone singlet to 9,10-diphenylanthracene is unlikely in view of the short lifetime of b-szophenone singlet. Moreover, fluorescence sensitization by benzophenone has not been observed[42]. It seems likely therefore that benzophenone competes with 9,10-diphenylanthracene in the same manner as pyrene for the available primary excitation energy. Benzophenone competes less effectively than pyrene, however, suggesting that transfer is not diffusion controlled.

Table I

Fluorescence Quantum Yields

Compound	Concentration (Moles/Liter x 10^7)	Solvent	Quantum Yield (%)
9,10-Diphenylanthracene	0.6	Ether[a] H_2O_2	54
9,10-Diphenylanthracene	1.9	Ether[a] H_2O_2	56
9,10-Diphenylanthracene	7.0	Ether[a] H_2O_2	76
9,10-Diphenylanthracene	70.0	Ether[a] H_2O_2	77
9,10-Diphenylanthracene	2000	Ether[a] H_2O_2	84
Pyrene	4250	Ether[a] H_2O_2	13
Fluorescein	5	Aqueous 0.1M Na_2CO_3	91.0
Fluorescein	20	Aqueous 0.1M Na_2CO_3[b]	48.0
Fluorescein	200	Aqueous 0.1M Na_2CO_3[b]	35.0
Fluorescein	2000	Aqueous 0.1M Na_2CO_3[b]	4.0
3,4-Dicarboxyacridone	50	Aqueous 0.1M Na_2CO_3[b]	13

[a] 1.17×10^{-1}M hydrogen peroxide in ether. Constant values of 84% were obtained in ether alone.

[b] These solutions contained both 3×10^{-2}M H_2O_2 and 6×10^{-2}M $K_2S_2O_8$.

Table II

Chemiluminescence Quantum Yields for Oxalyl Chloride-Hydrogen Peroxide Reactions

Concentrations (Moles per Liter x 10^5)		Quantum Yields (%)		
DPA[a]	Pyrene	DPA	Pyrene	Total
0.6	0	0.027	0	0.027
1.0	0	0.13	0	0.13
7.0	0	0.50	0	0.50
70.0	0	1.6	0	1.6
2000	0	2.0[b]	0	2.0
0	4250	0	0.047	0.047
0.6	4250	0.002	0.032	0.034
1.9	4250	0.003	0.043	0.046
7.0	4250	0.010	0.039	0.049
70.0	4250	0.11	0.047	0.16
Benzophenone				
7.0	4250	0.085	-	0.085

[a] 9,10-Diphenylanthracene

[b] Corrected for self-absorption. The uncorrected value was 1.3%.

B. Energy Transfer in 3-Aminophthalhydrazide Chemiluminescence

It was demonstrated in our previous report[2] that non-radiative energy transfer was essentially absent in aqueous 3-amino-phthalhydrazide chemiluminescence carried out in the presence of 4×10^{-4} molar disodium fluorescein. Energy transfer in this system, however, would be expected to require a collisional process, facilitated by high concentrations of the energy acceptor. We have therefore carried out a series of 3-aminophthalhydrazide-fluorescein experiments at fluorescein concentrations ranging up to 2×10^{-2} molar. The results are summarized in Table III.

Analysis of the results is complicated by two effects which operate at the higher fluorescein concentrations. (1) Self-absorption of fluorescein emission by fluorescein gives rise to seriously low observed emission values. Values which have been approximately corrected for self-absorption (see Experimental) are included in the table. Because of the approximate nature of the correction, however, these values must be considered semi-quantitative. (2) As seen in Table I, the fluorescence efficiency of fluorescein decreases rapidly as the fluorescein concentration increases. Since the chemiluminescence quantum yield of fluorescein emission is directly proportional to the fluorescence quantum yield of fluorescein, detection of energy transfer requires that the emission values be adjusted to a constant fluorescence efficiency basis. The adjusted values in Table III were obtained by dividing the corrected values by the fluorescein fluorescence quantum

yield at each concentration. The adjusted values thus represent the hypothetical chemiluminescence quantum yields corresponding to a constant fluorescein fluorescence efficiency of 100%.

The quantum gain denoted by the adjusted quantum yield values in Table III exceeds the uncertainty of the calculation and thus constitutes evidence of non-radiative energy transfer in the system. The relatively low maximum adjusted yield, however, suggests either (1) that energy transfer is insufficient from the 3-aminophthalhydrazide emitter, which might be caused by a short excited state lifetime, or (2) that the quantum yield of 3-aminophthalhydrazide chemiluminescence is limited by a low chemical yield of the emitting species.

While the preliminary results above are meaningful, it is clear that self-absorption and concentration quenching combine to make fluorescein poorly suited for energy transfer experiments at high acceptor concentrations. A search will be made for an acceptor less subject to adverse concentration effects so that quantitative energy transfer measurements can be made.

Table III

Energy Transfer in 3-Aminophthalhydrazide (3-AP)
Chemiluminescence in the Presence of Fluorescein (F)[a]

Fluorescein Concentration (Moles per Liter)	Quantum Yields (%)				
	3-AP Emission	F Emission			Total Adjusted Yield
		Observed	Corrected[b]	Adjusted	
Zero	1.08	-	-	-	1.08
2×10^{-5}	0.76	0.43	0.43	-	-
2×10^{-4}	0.34	0.67	0.67	1.4	1.7
2×10^{-3}	Trace	1.12	1.53	4.4	4.4
2×10^{-2}	Zero	0.08	0.15	4.0	4.0

[a] Reactions were run in $0.1\underline{M}$ aqueous Na_2CO_3 with hydrogen peroxide and potassium persulfate.

[b] Corrected for self-absorption, see Experimental

[c] Adjusted to a constant fluorescence efficiency basis. See Experimental.

Figure 1

CHEMILUMINESCENCE AND FLUORESCENCE SPECTRA OF 1×10^{-4} MOLAR 9,10-DIPHENYLANTHRACENE IN ETHER CONTAINING 1.17 MOLAR H_2O_2 AT $-10\,^\circ C$.

● — FLUORESCENCE BEFORE REACTION WITH OXALYL CHLORIDE

○ — FLUORESCENCE AFTER REACTION WITH OXALYL CHLORIDE

△ — CHEMILUMINESCENCE EMISSION OF REACTION WITH OXALYL CHLORIDE

Figure II

CHEMILUMINESCENCE AND FLUORESCENCE SPECTRA OF 1 X 10^{-3} MOLAR 9,10-DIPHENYLANTHRACENE IN ETHER CONTAINING 1.17 MOLAR H$_2$O AT -7°C.

● – FLUORESCENCE BEFORE REACTION WITH OXALYL CHLORIDE
○ – FLUORESCENCE AFTER REACTION WITH OXALYL CHLORIDE
△ – CHEMILUMINESCENCE EMISSION OF REACTION WITH OXALYL CHLORIDE

λ (mμ)

NORMALIZED EMISSION INTENSITY

Figure III

CHEMILUMINESCENCE AND FLUORESCENCE SPECTRA OF 4.25 X 10^{-2} MOLAR PYRENE CONTAINING
1.17 MOLAR H$_2$O$_2$ AT -10 °C.

O — FLUORESCENCE BEFORE REACTION WITH OXALYL CHLORIDE

● — CHEMILUMINESCENCE OF REACTION WITH OXALYL CHLORIDE

NORMALIZED EMISSION INTENSITY

λ (mμ)

Figure IV

ULTRAVIOLET ABSORBANCE CURVES FOR 9,10-DIPHENYLANTHRACENE (DPA) [0.7 X 10⁻⁴ M. DPA IN ETHER CONTAINING 1.1 X 10⁻¹ M. H_2O_2]

ZERO TIME BEFORE REACTION WITH OXALYL CHLORIDE

145 MIN. AFTER REACTION WITH OXALYL CHLORIDE
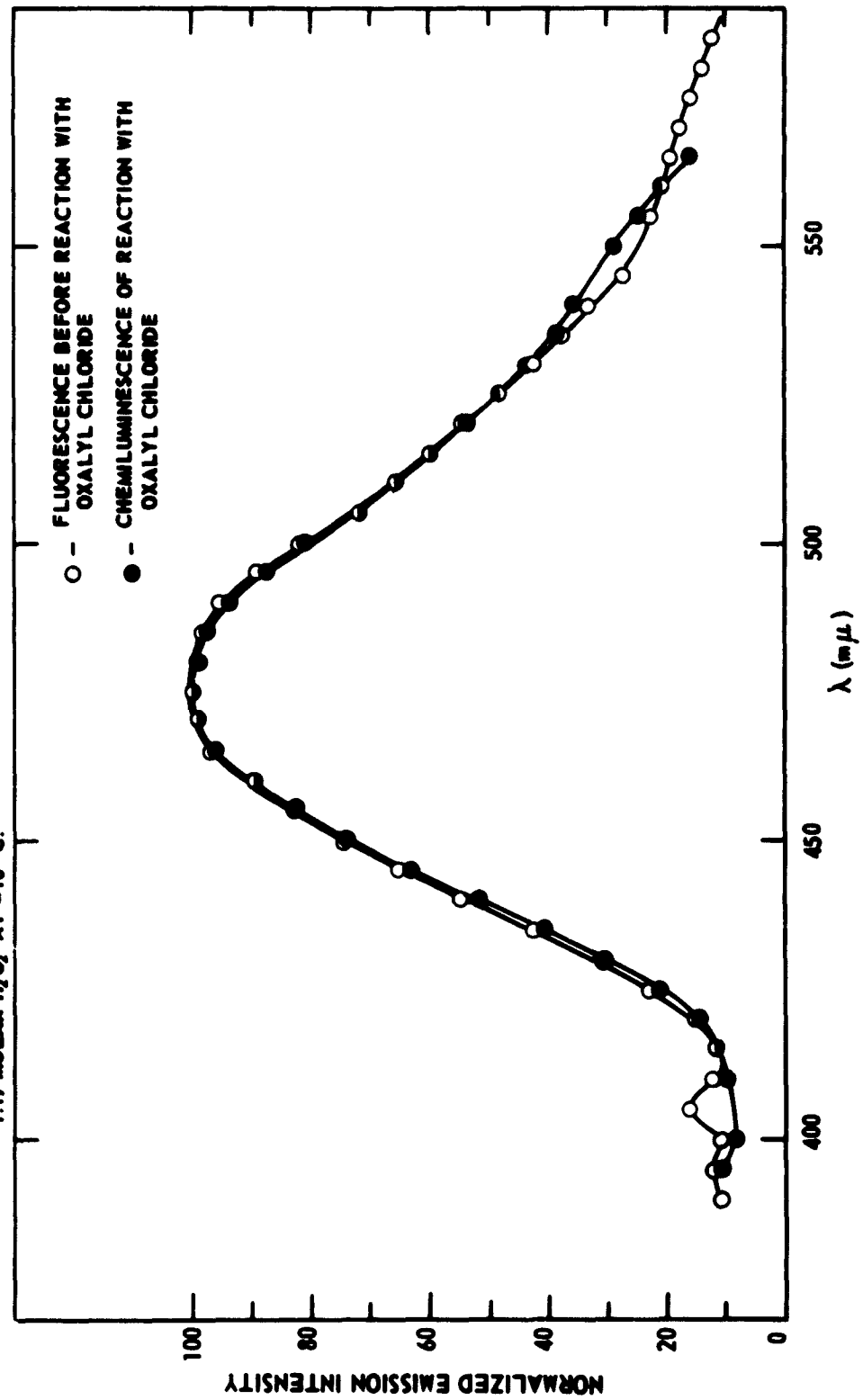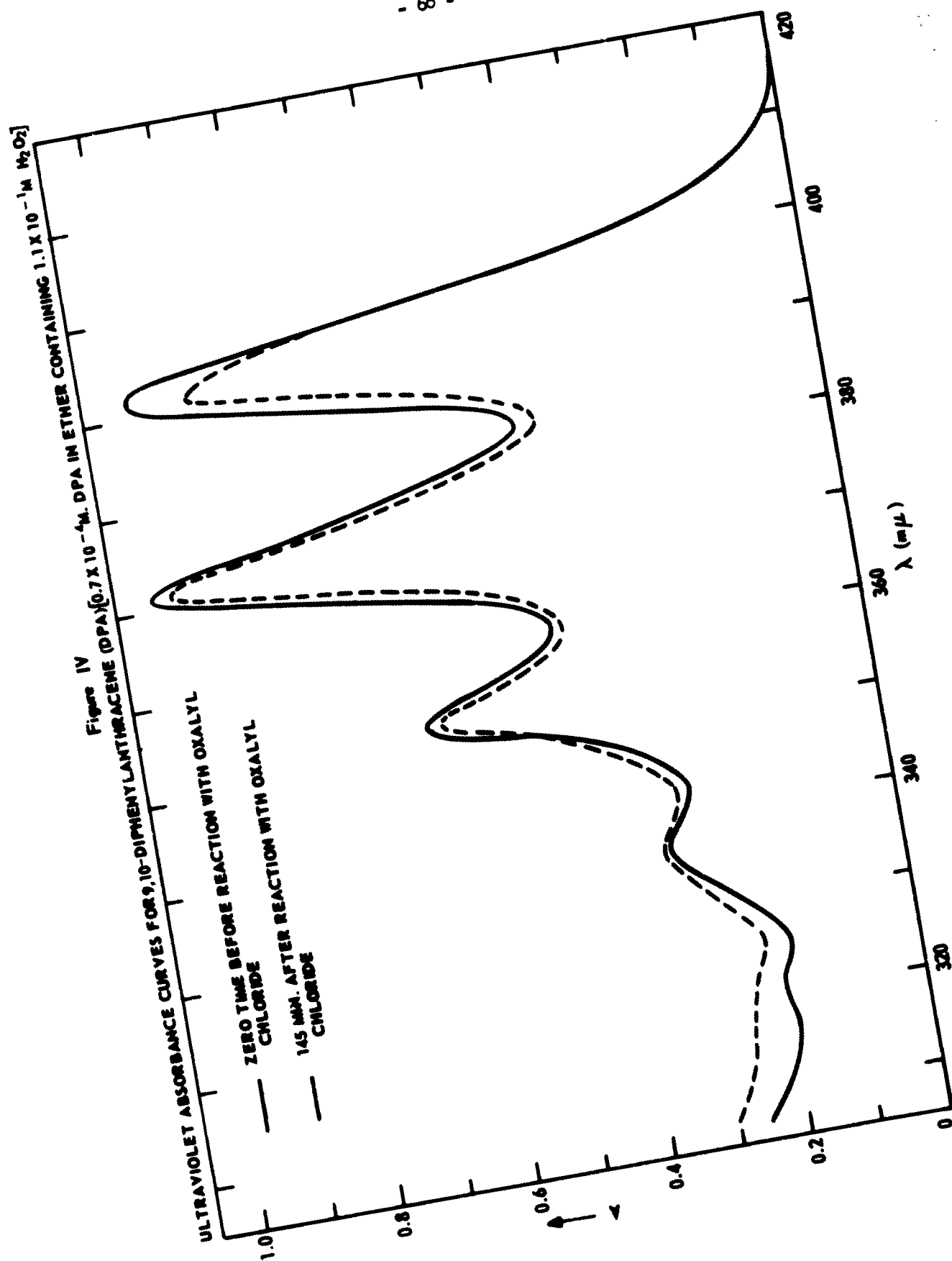
Figure V

CHEMILUMINESCENCE FROM OXALYL CHLORIDE AND HYDROGEN PEROXIDE
IN THE PRESENCE OF ACCEPTORS

(a) 9,10-DIPHENYLANTHRACENE (7 X 10^{-4} MOLAR)
(b) PYRENE (4.25 X 10^{-2} MOLAR)
(c) MIXTURE OF (a) AND (b)
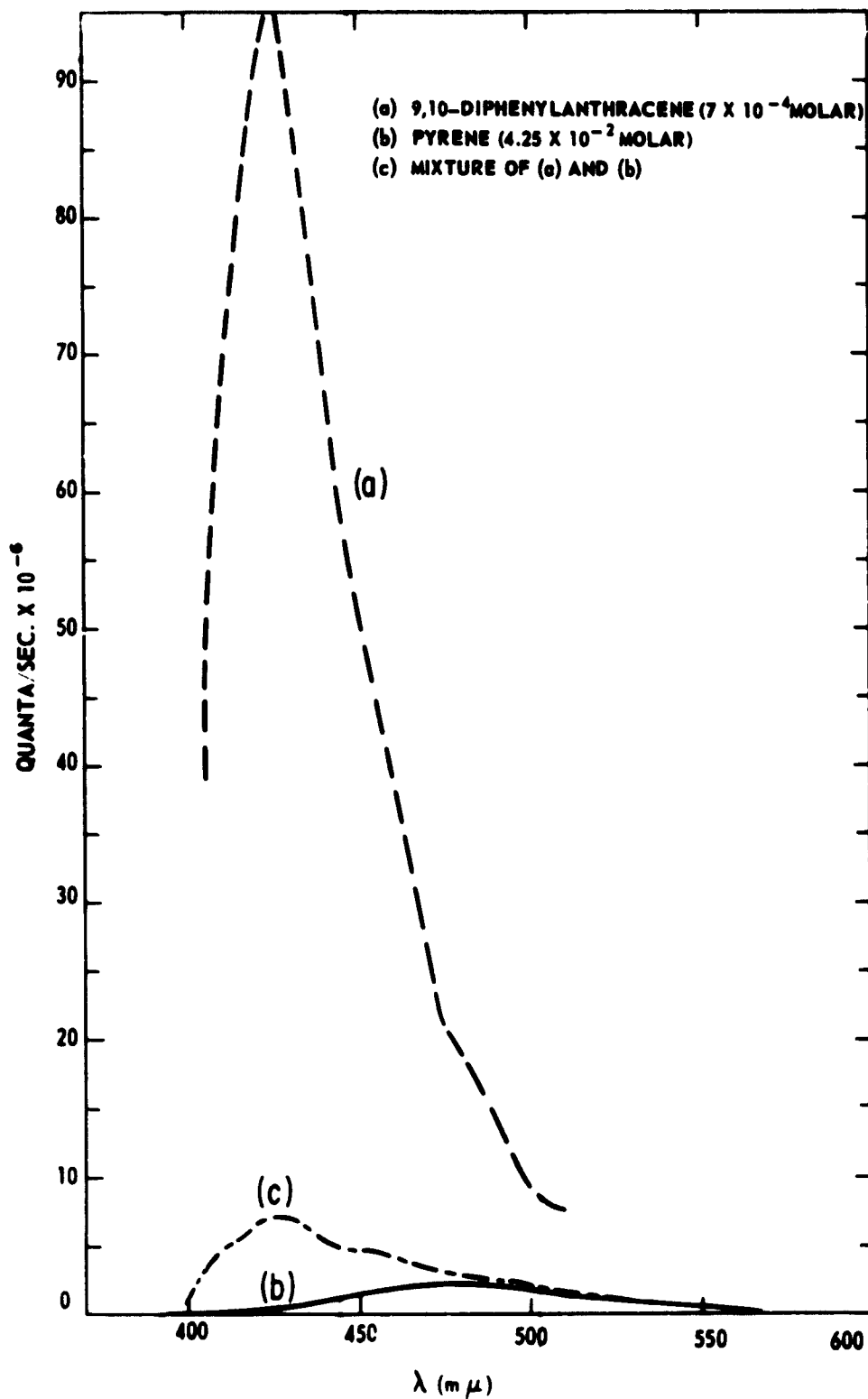
Figure Y!

REACTION RATE OF THE OXALYL CHLORIDE-HYDROGEN PEROXIDE-9,10-DIPHENYLANTHRACENE
CHEMILUMINESCENT REACTION IN ETHER AT 25°.

CONCENTRATIONS

OXALYL CHLORIDE: 0.94×10^{-2} MOLAR
H_2O_2 : 1.17×10^{-1} MOLAR
9,10-DIPHENYLANTHRACENE: 7.0×10^{-4} MOLAR

LOG INTENSITY

TIME (MIN.)
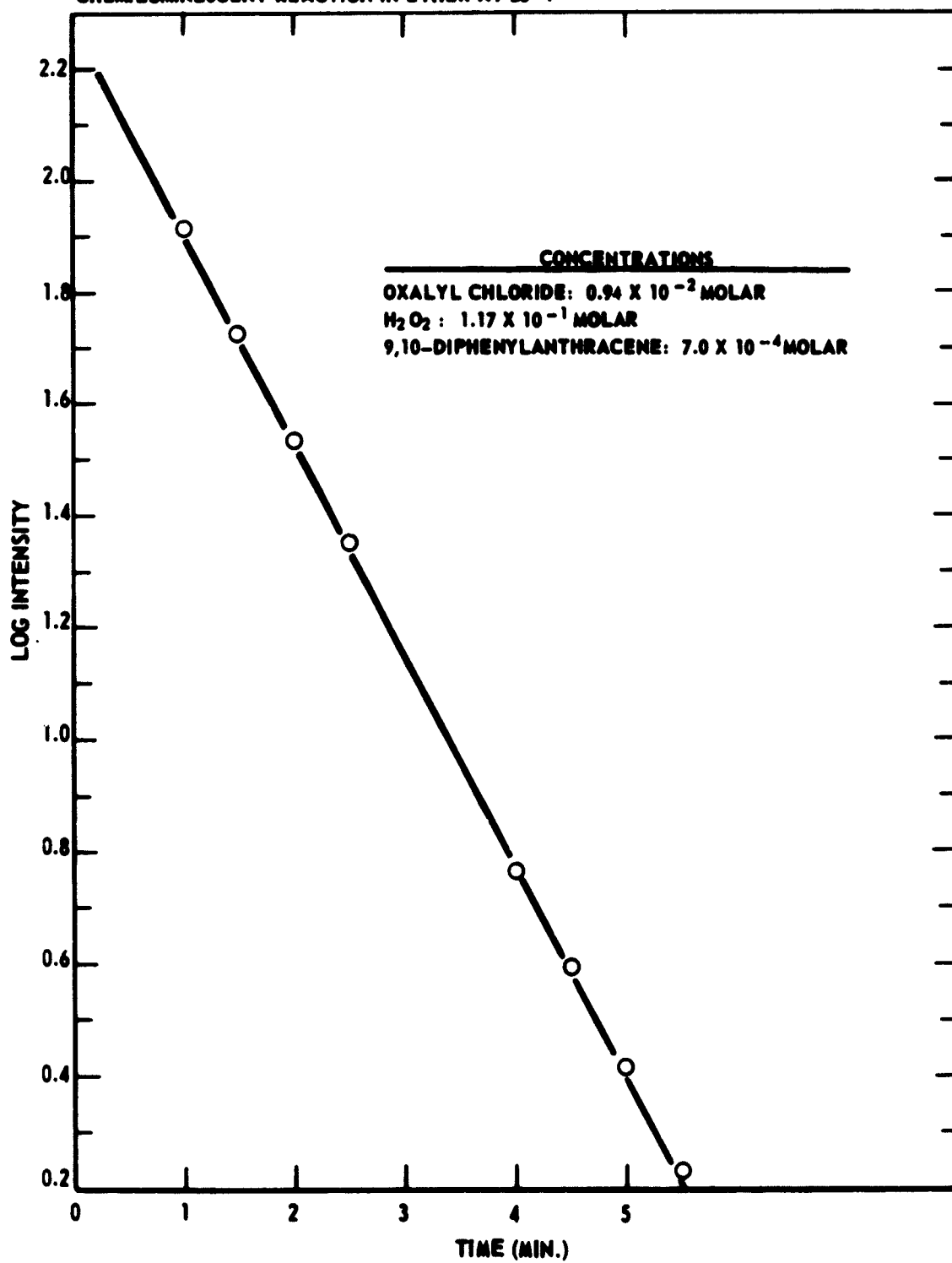
Figure VII

FLUORESCENCE SPECTRA OF 3,4-DICARBOXYACRIDONE AND OF COMPLETED HYDRAZIDE
OXIDATION REACTION

● – 5 X 10⁻³ M DICARBOXYACRIDONE

○ – ACRIDONE HYDRAZIDE OXIDATION PRODUCT
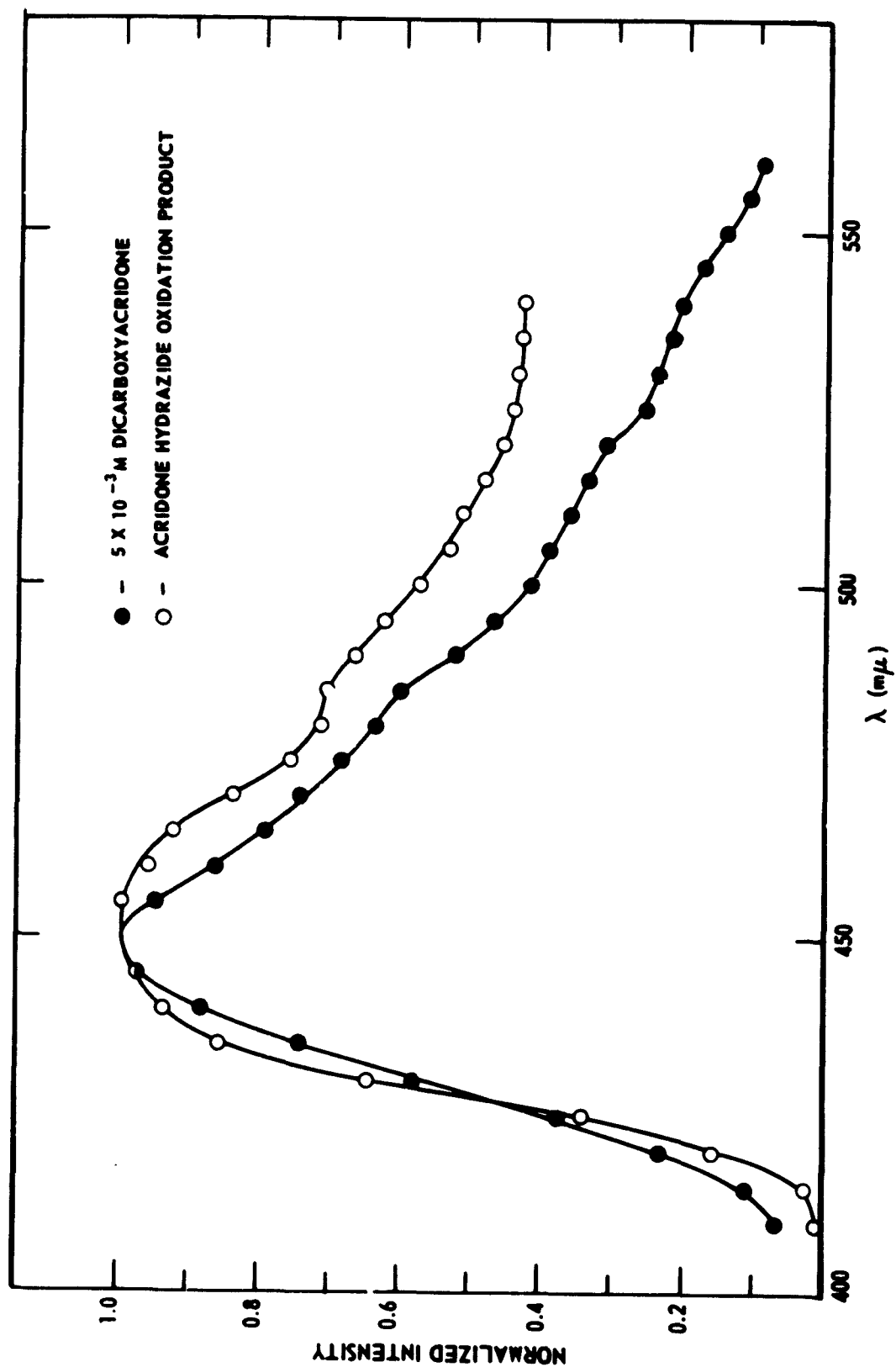
SECTION III

EXPERIMENTAL

Fluorescence Quantum Yield Measurements. The experimental
procedures and method for correcting the data have been described
previously[2] and were used without modification.

Chemiluminescence Quantum Yield Measurements of the Oxalyl
Chloride-Hydrogen Peroxide Reaction in the Presence of 9,10-Diphenyl-
anthracene and Pyrene. The experiments summarized in Table II were
carried out by injecting 0.040 ml. (0.27 mole) of 0.68M oxalyl chloride
in ether from a microsyringe into a solution of $1.17 \times 10^{-1}M$ hydrogen
peroxide and the fluorescent compound in ether contained in the quartz
cell of the radiometer. The final concentration of oxalyl chloride was
$0.94 \times 10^{-2}M$. The experiments were carried out at room temperature.
The spectral distributions of the emissions and intensity vs. time
measurements were carried out as described previously[2]. The reactions
were very fast with half-lives on the order of two minutes, and it was
necessary to correct the spectral distribution measurements for
intensity decay over the period of measurement. The computer was
programmed for this purpose. Typical spectral distributions are shown
in Figures I, II, III, and V. Beyond the first 30 seconds of reaction
the intensity decayed by a first order rate law. A typical intensity-
time plot is shown in Figure VI. Quantum yields were calculated from
the spectral distributions and decay data as described previously[2].

In the experiments where 9,10-diphenylanthracene and pyrene
were used together, the individual quantum yields for each acceptor
were calculated from the expression[2].

$$Q.Y._a = \frac{I^a_{\lambda ob}}{k' \left[\text{molecules of oxalyl chloride}\right] \dfrac{\int_{\lambda_1}^{\lambda_2} I^T_\lambda \, d\lambda}{I^T_{\lambda ob}}} \cdot \frac{\int_{\lambda_1}^{\lambda_2} I^T_\lambda \, d\lambda}{I^T_{\lambda ob}}$$

The spectral area terms $\dfrac{\int_{\lambda_1}^{\lambda_2} I^T_\lambda \, d\lambda}{I^T_{\lambda ob}}$ were determined from

experiments where the acceptors were used separately. λ_{ob} for 9,10-
diphenylanthracene was 405 mμ; λ_{ob} for pyrene was 540 mμ. A small
correction for pyrene emission at 405 mμ was necessary.

Detection of Energy Transfer in 3-Aminophthalhydrazide Chemi-
luminescence in the Presence of Fluorescein. The experiments summarized
in Table III were carried out as described previously[2] with reaction
mixtures containing 3-aminophthalhydrazide (4×10^{-3} molar), hydrogen
peroxide (3×10^{-2} molar), potassium persulfate (6×10^{-2} molar) and
varying concentrations of disodium fluorescein in 0.10 molar aqueous
sodium carbonate at 25°. The uncorrected quantum yield values were cal-
culated as described previously[2]. These values are erroneously low at
the two higher fluorescein concentrations because of self-absorption of
fluorescein emission by fluorescein. The values were approximately
corrected in the following way.

Fluorescence spectra and quantum yields were determined in
the usual way[2] for the concentrations of fluorescein used in the
chemiluminescence experiments (Table I). It was assumed that self-
absorption in the fluorescence experiments was negligible since front
surface excitation was used. (This assumption is only approximately
valid.) The ratio of the total quanta emitted throughout the spectral
distribution to quanta emitted at 590 mμ was calculated at each concen-
tration. Since self-absorption is serious only in the short wavelength
portion of the spectrum, it was assumed that the emission at 590 mμ in
the chemiluminescence experiments was substantially free from this
error. The 590 mμ:total spectral area ratio from fluorescence was then
used to correct the chemiluminescence spectral measurements by the
following relation:

Chemiluminescence quanta =

Chemiluminescence quanta at 590 mμ $\left(\dfrac{\text{Total fluorescence quanta}}{\text{Fluorescence quanta at 590 mμ}} \right)$

As seen in Table I, the fluorescence quantum yield for fluor-
escein decreases substantially as the concentration increases. Since
it is of interest to determine what the chemiluminescence quantum yield
would have been if the acceptor efficiency had remained constant, the
corrected chemiluminescence yields were adjusted by dividing by the
fluorescence quantum yield of fluorescein at each of the concentrations.
These values are included in Table III. The adjusted values are some-
what too high since the fluorescence yield measurements were not correc-
ted for self-absorption. However, the increase in adjusted yield with
concentration is significant.

Chemiluminescence Quantum Yield of 2,3-Dihydropyradazino/ 4,5-C 7
acridone-1,4,7-(12 H)trione. The emission from a reaction of the hydrazide
(1×10^{-3} molar), with potassium persulfate (6×10^{-6} molar), and hydrogen
peroxide (3×10^{-2} molar) in 0.1 molar aqueous sodium carbonate at 25° was

measured as previously described[2]. A plot of the log of the intensity vs. time was linear indicating a pseudo first order reaction. The reaction was long-lived, and the intensity was two low for an accurate estimate of the spectral distribution. For the quantum yield calculation[2], the spectral distribution of 3,4-dicarboxyacridone fluorescence was used. Little error was introduced with this approximation. The calculated quantum yield was 0.1%. The fluorescence spectrum of the spent chemiluminescence reaction mixture was found to be similar (Figure VII) to the fluorescence spectrum of the 3,4-dicarboxyacridone. From the intensity of fluorescence, it was estimated that about 10% of the starting hydrazide was oxidized to this compound.

Chemiluminescence Emission of Polymeric Hydrazide from Its Reaction with Potassium Persulfate and Hydrogen Peroxide in a 0.6 M Na$_2$CO$_3$ Solution. A mixture containing hydrazide polymer (3 x 10^{-2} equivalents of hydrazide per liter) 0.2M K$_2$S$_2$O$_4$ and 0.4M hydrogen peroxide in an aqueous solution of 0.6 M Na$_2$CO$_3$ was placed in the spectroradiometer fluorimeter[2] and the decay curve of the 430 mu band was recorded. The experiment was repeated with 4 x 10^{-3}M and 1 x 10^{-1}M solutions of the polymer and the same concentrations of K$_2$S$_2$O$_8$ and H$_2$O$_2$ as above. The intensities recorded at successive periods are summarized in the chart on page 45 in Section II.

The reaction mixtures became highly colored as reaction proceeded, particularly at the higher concentrations. Self-absorption thus contributed to the low efficiencies observed. All of the intensities were substantially lower than intensities obtained from 3-aminophthalhydrazide at 4 x 10^{-3} molar concentration.

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